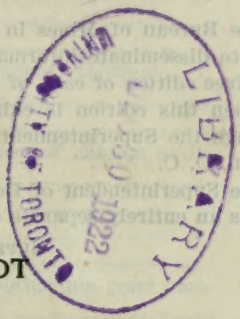
Gov. Doc.
U.S.
Mo.
U.S. Mines, Bureau

Technical Paper 265

DEPARTMENT OF THE INTERIOR
ALBERT B. FALL, SECRETARY
BUREAU OF MINES
H. FOSTER BAIN, DIRECTOR

MESOTHORIUM

TN
23
U63
no 265
ENGINEERING



BY

HERMAN SCHLUNDT

ENGIN STORAGE

WASHINGTON
GOVERNMENT PRINTING OFFICE
1922

TABLES.

		Page.
TABLE 1.	Constants of the thorium series	7
2.	Ratio mesothorium; thorium	11
3.	Ratio, MsTh : Th, in monazite sand; precipitation by means of aluminum hydroxide	14
4.	Ratio, MsTh : Th, for pure thorium nitrate solutions of known age and history (1–4 sulphate ppt., 5–7 aluminum hydroxide ppt.)	14
5.	Summary of the results obtained by McCoy and Henderson for the ratio, MsTh : Th	15
6.	Ratio, ThD : Th	16
7.	Experimental data on ratio, MsTh : Th	19
8.	Refining of crude concentrates of mesothorium	27
9.	Crystallization factors in bromide fractionations	35
10.	Higher fractionations of bromides (eighth series)	39
11.	Details of values taken out in tests of higher fractionations of bromides (eighth series)	39
12.	Relation of gamma-ray activity of mesothorium and radium	44
13.	Values for the constants K and K′	47
14.	Values for the constants K_1 and K'_1	48
15.	Rating of mesothorium, free from radium in terms of radium, at various ages, by absorption measurements with lead screens of different thicknesses	48
16.	Variations in the gamma-ray activity of mesothorium, free from radium, at various ages, by absorption in 0.5 cm. of lead	49
17.	Decay of radiothorium and mesothorium and growth of radiothorium in mesothorium in preparations	52
18.	Decay and growth of mesothorium 2 (λ=.112 hr.$^{-1}$)	53
19.	Decay and growth of thorium X (λ=0.00792 hr.$^{-1}$=0.190 d^{-1})	53

ILLUSTRATIONS.

		Page.
FIGURE 1.	Branching of thorium series	3
2.	Bromide crystallizing system	33
3.	Apparatus designed by Meyer and Hess for rating mesothorium	45
4.	Ionization chamber of the Meyer-Hess apparatus	46

PREFACE.

For a good many years the production of mesothorium in Germany, and to some extent in other countries in Europe, has kept pace with the production of radium.

The Germans early recognized the value of mesothorium as a substitute for radium, not only for luminous paint but also for medical purposes. Only during the last two or three years, however, has production taken place in this country.

Two companies have been recovering mesothorium as a by-product in the extraction of thorium. The Bureau of Mines has had a cooperative agreement with one of these companies, and Dr. Schlundt, the author of this paper, was responsible for the detailed work carried out in connection with this cooperation. Very little has been published concerning the recovery of mesothorium. Methods of measurement have been uncertain and somewhat difficult, and Dr. Schlundt's paper is a valuable contribution to the chemistry of this useful and interesting element.

R. B. Moore,
Chief Chemist, U. S. Bureau of Mines.

Digitized by the Internet Archive
in 2011 with funding from
University of Toronto

http://www.archive.org/details/technicalpaper265unit

MESOTHORIUM.

By Herman Schlundt.

INTRODUCTION.

Among the 30-odd radioactive elements, mesothorium, the first product of thorium, ranks next to radium in importance. Like radium, its disintegration products emit the three types of radiation that are characteristic of radioactive substances and that are known as alpha, beta, and gamma rays. Mesothorium decays at least 250 times faster than radium, and hence in the pure state its activity, weight for weight, would greatly exceed that of radium. Although itself rayless, its first product, which is rapidly formed after mesothorium has been separated, gives a powerful beta and gamma radiation; the alpha radiation of freshly prepared radium attains a maximum within a month, whereas that of mesothorium increases comparatively slowly, and reaches its high point during the fifth year after separation. Mesothorium preparations therefore must be "aged" before their full alpha-ray effect is realized in luminous products.

In the radium series one member, radium C, is mainly responsible for the gamma radiation. In the mesothorium series two members—the first product, mesothorium 2, and the final radioactive member, thorium D—emit gamma rays, those from thorium D being the most penetrating rays known. The maximum gamma activity is attained during the fourth year after separation, and its value is approximately 2.5 times that due to the mesothorium 2 present at the time. Consequently, during the first years of separation, notwithstanding the comparatively rapid decay of mesothorium, its preparations maintain a higher gamma-ray activity than an equivalent quantity of radium. Mesothorium may thus serve as a substitute for radium, both in luminous compounds of radium and for therapeutic purposes.

Uranium ores, especially carnotite, are worked primarily for the extraction of radium—uranium, vanadium, etc., being secondary products. Mesothorium, on the other hand, is obtained as a

secondary product or a by-product in the manufacture of thorium for the gas-mantle industry, its output being governed by the demand for thorium nitrate.

The quantity of mesothorium, unlike that of radium, is not expressed in milligrams by weight, but it is rated in terms of radium, the comparisons being made by the gamma-ray method. One milligram of mesothorium is that quantity of mesothorium 1, with its equilibrium amount of mesothorium 2, the gamma-ray activity of which is equal to the gamma-ray activity of 1 milligram of radium.

Mesothorium is identical with radium chemically, and both elements are closely analogous to barium. Mesothorium can not be separated from radium; therefore, radium extracted from uranium minerals containing thorium contains also mesothorium, and mesothorium separated from monazite sand usually owes approximately 20 per cent of its activity to the radium in the mineral. In a mineral containing equal proportions of uranium and thorium, the gamma radiation contributed by the radium is nearly six times as strong as that due to mesothorium alone, and nearly two and one-half times the total gamma radiation from mesothorium and its equilibrium products, when measured through 1.0 cm. of lead.

The methods used in extracting radium from its ores may be duplicated suitably in conserving the mesothorium in monazite sand. A little barium salt is added to the monazite sand during the treatment with sulphuric acid. The mesothorium and radium then follow the barium sulphate in the process of the recovery of thorium.

ACKNOWLEDGMENTS.

This report comprises a review of the published investigations on mesothorium with a list of references, and includes the results of the work on the extraction and recovery of mesothorium from monazite sand conducted during the year 1917–1918 at the Golden, Colo., station of the United States Bureau of Mines and at the plant of the Welsbach Co., Gloucester, N. J., later being continued for a time in the chemical laboratory of the University of Missouri.

The cooperative plan of investigation originated in 1917 with Dr. R. B. Moore, the director of the Golden station, and Dr. H. S. Miner, chief chemist of the Welsbach Co. The experimental work was conducted partly in the plant of the Welsbach Co. with the cooperation and direct supervision of Dr. H. S. Miner and Mr. S. Gulbrandsen. At the same time experiments were conducted in the Golden laboratory of the Bureau of Mines under the guidance of Dr. Moore and Dr. Lind. During the following year some experiments were conducted in the chemical laboratory of the University of Missouri to complete and extend certain parts of the investigation. The author

is pleased to express appreciation of the excellent cooperation given him in carrying on the experiments, and to acknowledge the help and good will of the younger members of the staff in the experimental laboratory and plant of the Welsbach Co. and of his colleagues in the Bureau of Mines.

CONSTANTS OF THE THORIUM SERIES OF ELEMENTS.

The thorium series of radio-elements comprise the following successive members: Thorium, mesothorium 1, mesothorium 2, radiothorium, thorium X, thorium emanation, thorium A, thorium B, thorium C, thorium C′, thorium D. Thorium C, like its corresponding member in the radium and actinium series, appears to have two modes of transformation. One branch, claiming 65 per cent of the atoms disintegrating, represents a beta-ray change, producing ThC′, which

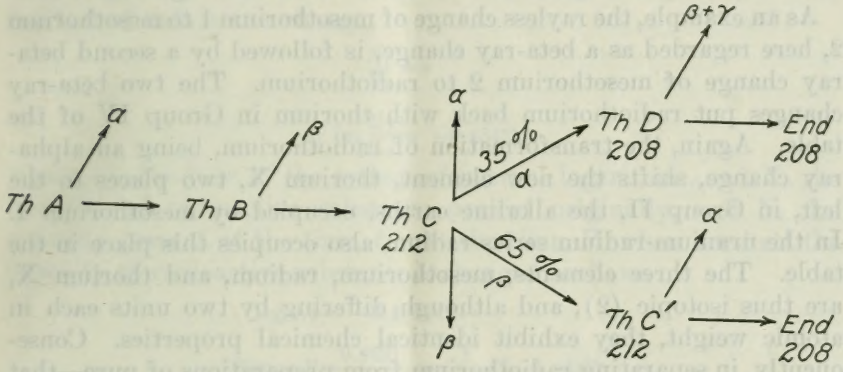


FIGURE 1.—Branching of thorium series.

changes almost at once with the expulsion of an alpha particle into the end member of this branch. The minor branch, claiming 35 per cent of the atoms, represents an alpha-ray change producing thorium D, which expels both beta and gamma rays, and is responsible for the entire gamma radiation emitted from the products of thorium C. This branching is shown in figure 1.

In the table of constants, Table 1, page 7, the elements of the thorium series are placed in their genetic order. The atomic weights and atomic numbers, following the experimental value for thorium, are theoretical values based upon the principle arrived at more or less independently by the several investigators, notably Soddy, Fleck, Russell, Fajans, and Von Hevesey (1)[a]—connecting the position of the radio-elements in the periodic table and their atomic weight with the nature of the radioactive change as the element is produced. The expulsion of the alpha particle, the nucleus of the helium atom

[a] Numbers refer to list of references, pp. 54 to 56.

(He ++), gives a new element the atomic weight of which is four units less than the parent atom, and its position in the periodic table is two places to the left. The expulsion of the beta particle, the unit negative charge, an electron, whether simple or accompanied by gamma radiation, causes a shift in position of one place from left to right, but no change in the atomic weight. The passage of the atoms successively produced through the periodic table thus goes backward and forward; as the alpha-ray changes are more numerous than the beta-ray changes and cause a shift of two places to the left to one toward the right for a beta-ray change, there is nevertheless a general resultant movement in the direction from right to left extending over ten places of the table from thorium to thallium. In part II of Soddy's admirable book, The Chemistry of the Radio-Elements, the place of each radio-element in the periodic table is shown by several diagrams, constructed on the above generalization.

As an example, the rayless change of mesothorium 1 to mesothorium 2, here regarded as a beta-ray change, is followed by a second beta-ray change of mesothorium 2 to radiothorium. The two beta-ray changes put radiothorium back with thorium in Group IV of the table. Again, the transformation of radiothorium, being an alpha-ray change, shifts the new element, thorium X, two places to the left, in Group II, the alkaline earths, occupied by mesothorium 1. In the uranium-radium series radium also occupies this place in the table. The three elements, mesothorium, radium, and thorium X, are thus isotopic (2), and although differing by two units each in atomic weight, they exhibit identical chemical properties. Consequently, in separating radiothorium from preparations of pure—that is, radium-free—mesothorium that have aged for a year or two, the mesothorium recovered also contains the thorium X present at the time. As thorium X produces successive alpha-ray products, such specimens of mesothorium exhibit an alpha-ray activity that decays to practically zero in the course of a month. The recovery in gamma-ray activity of such a specimen is very rapid during the first few days owing to the production of mesothorium 2, the maximum amount of which is present after an interval of three days. The initial rise in gamma-ray activity is augmented further by gamma radiation from thorium D resulting from the disintegration of the nonseparable thorium X. As thorium X decays to half value in 3.64 days, the gamma radiation of the specimen of mesothorium one month old is due almost entirely to mesothorium 2.

Freshly prepared specimens of mesothorium containing an equivalent of 20 to 25 per cent of radium sometimes fail during the first month to exhibit the normal rise in gamma-ray activity to be expected from their radium content. The explanation lies in the presence of

the isotopic thorium X, which decays at about the same rate that radium emanation accumulates in the sample of mesothorium, and thus in a measure compensates for the growth of radium C, the principal gamma-ray member of the radium series.

The column headed P, in Table 1, gives the period of half change, or simply the half period, which is the time required for one-half of the radioactive substance to change. Under λ we have the radioactive constant or transformation constant, expressing the time rate of change. The physical meaning of λ is the proportion, or fraction, of the total quantity of radioactive substance changing in the unit of time. The column headed L gives the period of average life, the reciprocal of λ.

The three constants, P, λ, and L are further related, L being 1.443P and $\lambda = \frac{1}{L} = \frac{0.6931}{P}$. These relations follow from the simple exponential law of radioactive change,

$$\frac{N_t}{N_o} = e^{-\lambda t}$$

$$\text{or } \log \frac{N_t}{N_o} = -0.4343\lambda t,$$

where e is the base of the system of natural logarithms, and N_o the quantity of radioactive substance present originally, and N_t the quantity present at the time, t. At the time, P, when one-half the quantity of radioactive substance is changed we have,

$$\log 0.5 = -0.4343\lambda P.$$

$$\text{Hence } P = \frac{0.6931}{\lambda}, \text{ or } \frac{1}{\lambda} = L = 1.443P.$$

The range, R, of alpha rays is the distance in centimeters through which ionization takes place in air. The values given are for air at 0° C. and 760 millimeters. The number of ions produced by the alpha particle in its path is proportional to $R^{2/3}$, that is, $N = a\ R^{2/3}$. The value for a, 70,080, used in the calculations, is based upon the work of Taylor (3) who found the whole number of ions produced by the alpha particle from polonium of range 3.58 centimeters to be 1.64×10^5. Finally the table of constants gives the absorption coefficients of the beta rays in terms of centimeters of aluminum, and of the gamma rays in terms of centimeters of lead, unless otherwise expressed. The significance of the numbers for the absorption coefficient may be seen by the following example. Assuming a simple exponential law for the absorption of beta and gamma rays as denoted by the equation,

$$I_t = I_o e^{-\mu t}$$

where I_o and I_t are respectively the intensities of radiation initially and after passage through any thickness t, and μ is the absorption

coefficient. The radiation is half absorbed in a thickness T given by $0.693/\mu$. The reciprocal of the absorption coefficient $1/\mu$ may be regarded as the "average path" of the individual rays. Although the above law of absorption is not always exactly followed, the absorption coefficients are convenient in calculating the approximate thickness of matter required to reduce the radiation to any desired fraction. Thus, the absorption coefficient for one of the groups of beta rays from mesothorium 2 being 20 centimeters of Al, $0.693/20=0.346$ millimeters of aluminum would reduce the intensity of the beta radiation to half value, and twice the thickness to one-fourth value. The coefficient of absorption for the gamma rays of mesothorium being 0.62 centimeters of lead, it follows from a similar calculation that 1.12 centimeters of lead will reduce the intensity of the gamma rays to one-half value and another screen of lead 1.12 centimeters thick will reduce the radiation to one-fourth value.

The experiments of Marsden and Darwin (30) and of Hahn and Meitner (31) established the conclusion that thorium C is a homogeneous member, whose atoms disintegrate in two ways. The period of half-change, given in Table 1—60.8 minutes—thus represents the period in which one-half of all the atoms in a given quantity of thorium C change by both modes of disintegration. The corresponding average life is 87.8 minutes. Assuming that each mode of this dual process proceeds independently, as in the case of a simple change, what is the half-period of each? Denoting the transformation constants by $\lambda\alpha$ for the 35 per cent branch, and $\lambda\beta$, for the 65 per cent branch, it follows that,[54]

$$\frac{1}{\lambda\alpha+\lambda\beta}=87.7 \text{ min. and } \lambda\alpha:\lambda\beta=35:65.$$

Solving for $\lambda\alpha$ and $\lambda\beta$ we obtain the values for L of 251 minutes for the 35 per cent branch, the alpha-ray change, and 135 minutes for the 65 per cent branch, values corresponding to half-periods of 174 and 93 minutes.

Recently Rutherford and Wood (55) by the scintillation method have detected the emission through thorium C of alpha particles with the exceptionally long range of 10.2 and 11.3 cm. in air at 15°. But this mode of disintegration of the atoms of thorium C is very rare, for only about 1 in 10,000 atoms gives rise to these very swift alpha particles.

RATIO OF MESOTHORIUM TO THORIUM AND OF THORIUM D TO THORIUM.

DEFINITION OF A MILLIGRAM OF MESOTHORIUM.

The researches of several investigators (33, 22) on the activities of thorium-bearing minerals and pure thorium compounds have defi-

TABLE 1.—*Constants of the thorium series.*[a]

Name symbol, atomic weight, group, atomic number.	Isotopes.	$\lambda=\frac{1}{L}$	$L=\frac{1}{\lambda}$	P	Alpha particle.		Beta and gamma radiation and absorption coefficient.
					R cm.	Total ions.	
Thorium, Th, 232.4, IV A, 90	RaTh.	5.3×10^{-11} yr.	1.9×10^{10} yr.	1.3×10^{10} yr. (1)	2.58 (8)	1.3×10^{5}.	
	UX_1.	3.7 do.	2.7 do.	1.86 do. (5).			
		3.9 do.	2.6 do.	1.78 do. (5).			
	Io.	4.6 do.	2.2 do.	1.5 do. (6).			
	RaAc.	2.9 do.	3.4 do.	2.3 do. (7).			
Mesothorium 1, MsTh1 (Ms1), 228.4, II A, 88.	ThX.	0.126 yr	7.9 yr	5.5 yr. (9, 10)			Rayless, or very soft beta rays.
	Ra.						
	AcX.	0.103 yr	9.7 yr	6.7 (7).			
Mesothorium 2, MsTh2 (Ms2), 228.4, III A, 89.	Ac.	0.112 hr	9.5 hr	6.2 hr (11)			$\mu\beta$=20 to 38.5 cm. Al (12). $\mu\gamma$=0.62 cm. Pb (13) $\mu\gamma$ RaC=0.5. $\mu\gamma$=0.116 cm. Al (14). $\mu\gamma$=0.75 cm. Pb (15) $\mu\gamma$ RaC=0.64 (15).
Radiothorium, RaTh (Rt), 228.4, IV A, 90.	Th.	0.364 yr	2.91 yr	737 d—2.02 yr. (16).	3.67 (8).		
	UX_1.			1.85—1.90 yr. (17)		1.66×10^{5}.	
	Io.			685 d—1.876 yr. (18)			
	RaAc.			696 d—1.905 yr. (7).			
Thorium X, ThX, 224.4, II A, 88	$MsTh_1$.			About 4 d (19).			
	Ra.	0.190 d.	5.27 d	3.65 d. (20, 21)	4.1 (22)	1.8×10^{5}.	
	AcX.			3.64 d. (22)	4.08. (8)		
Thorium emanation, ThEm, 220.4, 0, 86.	RaEm.			About 1 min. (23).	4.88 cm. (20)	2.02×10^{5}.	
				51.2 sec. (24).	4.74 (8)	1.92×10^{5}.	
	AcEm.	0.013 sec.		53.3 sec. (25).	4.74 (27)	1.92×10^{5}.	
		0.028 sec.		54 sec. (26).			

[a] The numbers in parentheses are references; see page 54.

TABLE 1.—*Constants of the thorium series*—Continued.

Name symbol, atomic weight, group, atomic number.	Isotopes.	$\lambda = \frac{1}{L}$	$L = \frac{1}{\lambda}$	P	Alpha particle.		Beta and gamma radiation and absorption coefficient.
					R cm.	Total ions.	
Thorium A, ThA (A), 216.4, VI B, 84....	Th C_1. Ra A. Ra C_1. Ra F. Ac A. Ac C_1.	4.95 sec.....	0.20 sec.....	0.14 sec. (28).....	5.1 (27)..... 5.4 (8).....	2.08×10^5. 2.16×10^5.	
Thorium B, ThB (B), 212.4, IV B, 82....	Pb. Ra B. Ra D. Ac B.	0.0654 hr.....	15.3 hr.....	10.6 hrs. (20, 22)...	.....	.....	=110 cm. Al (12).
Thorium C, ThC (C), 212.4, IV B, 83...	Bi. Ra C. Ra E. Ac C.	0.0118 min.....	87 min.....	60.4 min. (20).....	4.55 cm. (8)....	1.92×10^5.....	=14.4 cm. Al.
(65 per cent β.) Thorium C^1, ThC^1 (C^1), 212.4, VI B, 84. (35 per cent α.)	Th A. Ra A. Ra C_1. Ra F. Ac A. Ac C_1.			10^{-11} sec.	8.16 (8).	2.84×10^5. Th C+Th C^1. 2.52×10^5.	
(65 per cent α.) Thorium D, ThD (D), 208.4, III B, 81. (β and γ.)	Tl.....	0.224 min.....	4.5 min.....	3.1 min.....	.....	.....	$\mu\beta$=21.6 cm. Al $\mu\gamma$=0.096 Al (14) 0.092 cm. Al (13) $\mu\gamma$=0.463 Pb (13) $\mu\gamma$=0.58 Pb (15) $\mu\gamma$ Ra C=0.64
End product, Pb (Th), 208.4, 82, IV B. End product, Pb (Th), 208.4, 82, IV B.	Pb (or d). Pb (Ra).						

nitely established that the alpha-ray activity of a mineral is proportional to its thorium content, corrections being made for any radium and uranium present. This result proves that, as a member of the thorium series, mesothorium, although not emitting alpha rays, bears a fixed ratio to thorium in minerals. Pure mesothorium, however, has never been obtained. The product from monazite sand, even when fully as active weight for weight as radium, contains only about one-fourth of 1 per cent of mesothorium by weight, practically the entire mass being barium and radium compounds. Likewise specimens of mesothorium free from radium prepared chemically from mantle ash, are barium compounds, the quantity of mesothorium constituting a mere trace. Notwithstanding the minute mass of mesothorium in such preparations, its relatively rapid rate of decay imparts to them a gamma-ray activity comparable to that of radium. The custom has thus grown up of expressing the quantity of mesothorium not, as with radium, in milligrams by weight, but by its gamma-ray activity. One milligram of mesothorium is the quantity of mesothorium 1 with its equilibrium amount of mesothorium 2, whose gamma-ray activity is equal to that of one milligram of radium, containing the equilibrium amounts of its short-lived products.

Mesothorium 2 is present in equilibrium amount in freshly prepared specimens of mesothorium after an interval of three days. As mesothorium, radium, and thorium X are isotopes, all new preparations of mesothorium from thorium minerals contain also radium and thorium X. For this reason, the beta and gamma activity of new mesothorium are variable during the first month. By the end of this time, radium emanation and its short-lived products have attained equilibrium, when the specimens are kept in sealed tubes, and thorium X and its products have practically decayed. During this interval a small quantity of radiothorium forms, which determines the amount of another gamma-ray product, thorium D. The increase in gamma-ray activity from this source more than compensates for the decay of mesothorium, as is shown in the table for the growth of radiothorium in mesothorium preparations (see Tables 16 and 17 (pages 49, 52). Finally, as the gamma radiation of mesothorium 2 is somewhat less penetrating than that from radium C (see table of constants, p. 7) the activity of mesothorium preparations depends to some extent on the thickness of the lead screen interposed in making comparison measurements. In standardizing commercial specimens of mesothorium the gamma-ray comparisons are made from 30 to 40 days after separating and sealing the specimens, the ionization chamber of the electroscope being screened by 1 centimeter of lead. At this time the gamma-ray effect of the thorium D

that has accumulated during the interval amounts to about 4 to 5 per cent. The rating of mesothorium of various ages in terms of radium is discussed more fully on page 43.

MESOTHORIUM: THORIUM RATIOS.

The actual quantity of mesothorium associated with a known weight of thorium in a mineral can be deduced on the principle of radioactive equilibrium. The number of atoms of mesothorium produced per second by thorium is equal to the number transformed. This relation is generally expressed thus: $\lambda_1 N_1 = \lambda_2 N_2$, where λ_1 is the radioactive constant of thorium and N_1 the number of atoms of thorium under consideration, λ_2, the radioactive constant of mesothorium, and N_2, the number of atoms of mesothorium in equilibrium.

When the equilibrium relation is expressed in actual weights the equation takes the form,

$$\frac{Q_2}{Q_1} = \frac{228\lambda_1}{232\lambda_2}$$

Since Q_1 can be calculated from the percentage of thorium in the mineral as determined by chemical analysis and the radioactive constants are known, the actual quantity of mesothorium can be computed. Furthermore, if it is assumed that the gamma rays from mesothorium and radium produce the same amount of ionization, atom for atom, the radium equivalent of mesothorium will be given by multiplying the equilibrium quantity Q_2 by the ratio of their transformation constants, or the ratio of their half periods, 1690 and 6.7 years, namely, 252.

The values for the radioactive constant of thorium, as shown in Table 1, although of the same order of magnitude, show considerable variation. The values for the ratio, mesothorium: thorium, corresponding to the several constants are given in Table 2. The numbers in the third column express the ratio in terms of radium equivalent, obtained by multiplying the values in the second column by 252. The fourth column gives the reciprocal of the ratios in the third column, namely, the weight in grams of thorium in equilibrium with one milligram of mesothorium expressed as radium. The experimental values of McCoy and Henderson (35) and the ratio based upon the author's experiments have been included in the table. In the last column are recorded the milligrams of mesothorium per ton (2,000 lbs.) of monazite sand containing 6 per cent thorium oxide. The calculation of Kithil (34) for the quantity of mesothorium per ton of monazite sand assumes that the gamma-ray activities of mesothorium and radium are inversely proportioned to their half periods. Meitner's half-time period of mesothorium, 6.7 year $\lambda = 0.103$. has been used in the author's calculations.

TABLE 2.—*Ratio, mesothorium: thorium.*

Radioactive constant of thorium.	Weight ratio, MsTh : Th.	Ratio, MsTh : Th as Ra. equivalent.	Ratio, Th : MsTh as Ra. equivalent.	MsTh per ton monazite, 6 per cent ThO_2 (mgs).
5.3×10^{-11} yr. (4)	5.06×10^{-10}	1.27×10^{-7}	7.85×10^{6}	6.09
3.7×10^{-11} yr. (5)	3.53×10^{-10}	0.89×10^{-7}	11.2×10^{6}	4.25
3.9×10^{-11} yr. (5)	3.73×10^{-10}	0.94×10^{-7}	10.7×10^{6}	4.49
4.6×10^{-11} yr. (6)	4.39×10^{-10}	1.11×10^{-7}	9.04×10^{6}	5.29
2.9×10^{-11} yr. (7)	2.77×10^{-10}	0.697×10^{-7}	14.3×10^{6}	3.33
.....	.....	0.524×10^{-7} (35)	19.0×10^{6}	2.52
.....	.....	0.60×10^{-7}	16.7×10^{6}	2.87

The experimental value of the ratio, Th : MsTh, which McCoy and Henderson found to be 19×10^{6}, is the weight in grams of thorium in equilibrium with one gram of mesothorium, a gram of mesothorium being the quantity that has a gamma-ray activity of one gram of radium element. That experimental ratio exceeds the highest theoretical value by 30 per cent, and is more than double the ratio based upon the count by Geiger and Rutherford (4) of the number of alpha particles emitted by thorium. As the uranium radium ratio is very closely 3.0×10^{6}, it takes six times as much thorium in a mineral per milligram of mesothorium as uranium per milligram of radium.

EXPERIMENTAL DETERMINATION OF THE RATIO, MESOTHORIUM : THORIUM.

McCoy and Henderson (35), and also the author of this paper, have conducted experiments to establish the ratio of mesothorium to thorium in minerals. Owing to the large quantity of mineral necessary to give enough mesothorium for accurate measurement by the gamma-ray method, McCoy and Henderson devised an indirect comparison with the gamma activity of radium. In the author's experiments on the extraction and recovery of mesothorium from monazite sand the gamma-ray activities were compared directly.

The method followed by McCoy and Henderson was to determine the beta-ray activity of the mesothorium extracted from a known amount of thorium, and then to measure for pure mesothorium; that is, for mesothorium free from radium, the ratio of beta to gamma activity. The beta activity of mesothorium could then be expressed in units of gamma activity, and knowing the gamma activity in terms of radium, the amount of thorium in equilibrium with 1 milligram of mesothorium could be calculated. The result for the ratio of mesothorium: thorium, 0.524×10^{-7}, appears in Table 2. As the experimental ratio falls below the theoretical value based upon an atom-for-atom equivalence of ionization by gamma rays, the conclusion is hardy warranted that the gamma rays of

mesothorium and radium are emitted atom for atom. However, in comparing the experimental value with the calculated ratio based upon the half period of thorium recently found by Meitner (7), the difference may be explained by the greater absorption of the gamma rays of mesothorium in the lead screens interposed when comparison measurements were being made with radium.

The author's experiments have led him to assign a value not greater than 16.7×10^6 to the ratio, thorium : mesothorium.

EXPERIMENTS OF MCCOY AND HENDERSON (35).

McCoy and Henderson separated mesothorium quantitatively from the minerals thorianite and monazite sand, and from pure thorium nitrate solutions by several methods, and then made the necessary measurements of activity a month or more after separation. Two procedures were followed: In the first, the total beta activity of a barium sulphate film was measured and correction was made for the activity due to radium, the amount of which was determined by the emanation method. In the second method—the one used in all except the preliminary experiments—the active barium sulphate was converted into chloride, and after an interval of a month, the pure mesothorium 2 was separated from a solution of chloride and its beta-ray activity was measured.

The beta-ray measurements were made with a gold-leaf electroscope, the bottom of whose ionization chamber was made of 0.05-cm. aluminum. The films were placed 5 cm. below the aluminum screen, and all measurements were made by comparison with a constant arbitrary standard.

The gamma-ray measurements were made through 2.03 mm. of lead and 1.32 mm. of brass, in terms of a radium standard, by placing the films or precipitates in a circular lead dish resting on the top of a brass electroscope.

To find the factor for converting the arbitrary beta units of mesothorium 2 into the gamma activity of 1 mg. of radium, a radium-free solution of mesothorium 1 was divided accurately into two portions containing the mesothorium in the approximate ratio of 90 to 1. The smaller portion was used for beta-ray measurements, the larger one for gamma activity in terms of a radium standard. Mesothorium 2 was separated quantitatively from the two solutions by precipitating aluminum hydroxide in them. Knowing the relative amounts of mesothorium 1 in each solution and the gamma activity of the stronger in terms of radium, and the beta activity of the other in arbitrary beta units, one could calculate the number of arbitrary beta units that are equivalent to the gamma activity of 1 mg. of radium or mesothorium, when the gamma rays from the mesothorium are

due entirely to mesothorium 2. For the electroscope used, the average value of several determinations gave 278 arbitrary beta units of mesothorium 2 equivalent to the gamma activity of 1 mg. of radium element.

McCoy and Henderson carried out the quantitative extraction of mesothorium from the mineral thorianite by two methods: The precipitation of iron and barium as carbonates, in the nitric acid solution (22), and the precipitation of barium as sulphate in the solution, as described by Soddy (36).

In the separation of mesothorium from monazite sand, hot concentrated sulphuric acid was used to decompose the ore. When a little barium salt was present, the small insoluble residue that remained when the product was dissolved in cold water contained practically all the mesothorium. By boiling the residue successively with portions of sodium carbonate, the barium and mesothorium were converted into carbonates. After converting the carbonates into chlorides, the barium was again precipitated as sulphate to remove some phosphoric acid that remained. To convert the sulphate into chloride the precipitate was fused with mixed carbonates of sodium and potassium, and the washed carbonate dissolved in hydrochloric acid. This solution was free from phosphoric acid and the mesothorium could be determined by the aluminum hydroxide method of separating mesothorium 2.

Finally McCoy and Henderson obtained the ratio of mesothorium to thorium in pure thorium nitrate solutions free from radium and of known age and history. Knowing the decay constant for mesothorium, the fraction of the total equilibrium amount of mesothorium in these solutions could be calculated from the formula, $MsTh = 1 - e^{-\lambda t}$, where λ is the radioactive constant of mesothorium and t the age in years. In the experiments with these solutions two methods of extraction of mesothorium were followed. In the first method, the mesothorium was obtained in the filtrate by precipitating the thorium with ammonia after adding a little barium chloride. To secure the complete removal of the mesothorium from the thorium hydroxide, the precipitate was dissolved in hydrochloric acid and reprecipitated, and this operation was repeated five to six times. From the combined filtrates the mesothorium and barium were precipitated as sulphate which was employed, in the form of films, for the beta-ray measurements.

In the second method of separating mesothorium from the thorium nitrate solutions, barium was precipitated as sulphate. The sulphates were then converted into carbonates by fusion with sodium and potassium carbonate, and then into chlorides. The activity of the result-

ing solution was determined as mesothorium 2 with aluminum hydroxide.

Some of the experimental data given by McCoy and Henderson for the ratio of mesothorium to thorium in monazite and pure thorium nitrate are reproduced in Tables 3 and 4, and a summary of all values is given in Table 5.

TABLE 3.—*Ratio, MsTh: Th in monazite sand; precipitation by means of aluminum hydroxide.*

Grams of thorium.	Beta activity at time zero.	Beta activity per gram of Th.	MsTh : Th×10^7.
39.24	0.555	0.01415	0.509
39.24	.585	.0149	.536
39.24	.535	.01363	.491
39.24	.535	.0136	.491
28.83	.387	.01345	.484
		Average.	.502

The MsTh : Th ratio in the last column is obtained by dividing the beta activity per gram of thorium by 278, the $\frac{\beta}{\gamma}$ ratio, and by 1,000 to convert milligrams of mesothorium into grams.

TABLE 4.—*Ratio, MsTh: Th, for pure thorium nitrate solutions of known age and history (1–4 sulphate ppt., 5–7 aluminum hydroxide ppt.)*

Age of sample (years).	Gr. of thorium.	Activity of ppt.	$1-e^{-\lambda t}$ Th solution.	Beta activity per gr. Th in equilibrium.	MsTh : Th × 10^7. [a]
3.633	15.397	0.0945	0.3687	0.01656	0.596
3.625	13.375	.0806	.3687	.01634	.588
3.875	16.785	.0919	.3863	.0142	.511
3.952	14.61	.0868	.393	.0151	.543
5.75	59.85	.445	.5158	.0143	.516
5.3	45.58	.300	.4872	.0136	.490
5.792	25.99	.1946	.5181	.01446	.520

[a] Average.....0.538 × 10^{-7}.

In arriving at the beta activity per gram of thorium in equilibrium, the observed activity is divided by the value of $1-e^{-\lambda t}$, in which occurs the radioactive constant, $\lambda=0.126$, corresponding to a period of half change of 5.5 years for mesothorium. Employing instead the value 0.103 obtained by Meitner (7) corresponding to a half period of 6.7 years in the calculations, an average of experiments 1 to 4 inclusive gives the value 0.632×10^{-7}, for the ratio, and a value 0.580×10^{-7}, as an average of experiments 5 to 7, values somewhat higher than the ratios found by the other methods, all of which are summarized ing the following table:

TABLE 5.—*Summary of the results obtained by McCoy and Henderson for the ratio, MsTh: Th.*

No.	Source.	Method.	MsTh: Th. $\times 10^7$.
I.	Thorianite	$BaSO_4$	0.555
II.	do	$Al(OH)_3$	.535
III.	Monazite	$Al(OH)_3$	.502
IV.	Pure thorium nitrate	$BaSO_4$	.559
V.	do	$Al(OH)_3$	.508
	Average		.531

The reciprocal of the average ratio, 18.8×10^6 is the weight in grams of thorium in equilibrium with one gram of mesothorium defined as the quantity that has a gamma activity equivalent to the gamma activity of one gram of radium. As the ratio of uranium to radium corrected to the new international standard (37) is 3.1×10^6 it is seen that the ratio of thorium to mesothorium is only one-sixth as great.

GAMMA-RAY ACTIVITY OF THORIUM D.

The recent determinations by McCoy and Cartledge (38) of the ratio of thorium D to thorium reveal an interesting relation. As a result of two series of experiments they found that the gamma activity of the thorium D in equilibrium with 1 gr. of thorium is equal to 0.956×10^{-7} grams of radium. They point out that if with this ratio is combined the above ratio of mesothorium to thorium, 0.53×10^{-7}, the result is 1.49×10^{-7} gr. as the radium equivalent of the gamma-ray products of thorium, determined separately, a figure in agreement with the experimental value of 1.46×10^{-7} by McCoy and Henderson for the total gamma activity per gram of thorium in thorianite.

Finally, it is important to add, McCoy and Cartledge noted, that thorium D furnished 1.80 times as much gamma activity as the mesothorium with the same amount of thorium. As only about 35 per cent of the thorium disintegrated into thorium D, this means that thorium D contributed 5.14 times as much gamma activity as mesothorium. The investigators therefore conclude, "this result shows conclusively that an atom-for-atom relation does not hold for gamma radiation." It is far more probable, they say, that the intensity of the gamma radiation is related closely to the speed of the accompanying beta rays.

For the determination of the gamma-ray activity of thorium D, Cartledge (42) first perfected a method for the quantitative estimation of thorium by means of the emanation. McCoy and Cartledge then undertook the determination of the ratio ThD: Th. They

separated enough radiothorium from a sample of active mesothorium for a determination of its gamma-ray activity by direct comparison with a radium standard. The measurements were made on an aliquot part of the radiothorium solution after a period when thorium X had attained equilibrium with the radiothorium. Other aliquot portions of the original solution were diluted largely in stages until a convenient sample containing the equivalent of about 0.25 gram of thorium was obtained. On these samples emanation determinations were made using as standards in different tests solutions of thorianite and monazite of known thorium content. In this way the thorium equivalent of a given quantity of thorium D measured against a radium standard was obtained in two series of experiments in which the procedures differed somewhat. The results are summarized in Table 6. The measured gamma activity of the thorium D is given in the first column, then follows the thorium equivalent, and finally the ratio ThD : Th.

TABLE 6.—*Ratio, ThD : Th.*

ThD $\times 10^{4}$g.	Th equivalent.	ThD: Th. $\times 10^{7}$.
0.144	153.4	0.94
.824	844	.98
5.18	5,802	.89
3.81	3,868	.98

Weighted mean, ThD : Th = 0.956×10^{-7}.

RATIO OF MESOTHORIUM TO THORIUM BY DIRECT COMPARISON OF GAMMA ACTIVITY WITH RADIUM.

The experiments of the Bureau of Mines embraced two plant runs, each with about five tons of monazite sand of known thorium content. The treatment of the ore was conducted in the plant of the Welsbach Co., Gloucester, N. J., under the direct supervision of Messrs. Gulbrandsen and Nonnemaker, members of the research staff of that firm. A careful record was kept of the quantities of ore used, the amounts of reagents used, the volumes of liquors in the different stages, and the weights of the products separated. Samples of these products together with the entire quantity of crude sulphates of barium containing the mesothorium were then sent to the laboratory of the United States Bureau of Mines, Golden, Colo., where the author conducted most of the analyses and radio-active measurements. Expressing the ratio, as is customary, in terms of the gamma-ray activity of radium, revealed that one gram of mesothorium was in equilibrium with 16.7×10^{6} grams of thorium in Brazilian monazite sand. In other words, one gram of thorium contained mesothorium whose gamma activity corresponded approx-

imately to 6×10^{-7} grams of radium. This ratio of thorium to mesothorium, though of the same order of magnitude, is greater than the theoretical value of Table 2, based upon the life periods, but it stands in fairly good agreement, with the value 18.80×10^{6}, found by McCoy and Henderson (35), though it is somewhat lower.

EXTRACTION OF THORIUM FROM MONAZITE SAND.

In the first run, crystallized barium chloride equal to one-half of 1 per cent of the weight of the ore was added before decomposing the monazite by boiling it in hot concentrated sulphuric acid; in the second run only 1 pound of barium chloride was added for each 400 pounds of ore. After cooking with sulphuric acid the product was mixed with water and diluted further with vigorous stirring. In this operation the mesothorium was precipitated quantitatively with barium as sulphate. The barium sulphate bearing the mesothorium and radium thus accompanied the thorium and other rare earths, and was removed, or slimed off from the unattacked impurities in the sand, remaining as a sediment in the tank. By this method of treatment 4 to 6 per cent of the mesothorium remained with the coarse, unattacked mineral in the sand.

The solution carrying the sulphates and phosphates of thorium, with the other rare earths, was then treated for the separation of thorium which settled out as a phosphate, together with small portions of the associated rare earths. The mesothorium, radium, and barium sulphates accompanied the thoria phosphate, and in the subsequent process of purification the barium sulphate followed the thorium until the latter was converted into chloride. As the process of the recovery of the thorium involves several treatments and washings before the thorium is finally converted into chloride, the losses of barium sulphate in the wash liquors may assume considerable proportions. The insoluble residue remaining in the impure thorium chloride liquor constituted the crude concentrate of mesothorium. It was filtered off, washed several times, and then dried.

EXAMINATION OF CRUDE CONCENTRATE.

To obtain the ratio of mesothorium to thorium the following data are required: The percentage of thorium in the monazite sand used, the percentage of recovery of mesothorium in the crude concentrate, and the gamma activity of a known weight of the concentrate in terms of radium from which the total gamma activity of the concentrate is computed and expressed in milligrams of radium equivalent. Dividing this total activity by the percentage of mesothorium recovered gives the total mesothorium in the ore used, correction being

made for the radium content of the ore and the concentrate. The ratio then follows directly by dividing the mesothorium activity (gamma) by the total thorium in the charge. A correction must be introduced for the gamma activity of the thorium D which has accumulated in the crude concentrate during the interval between its separation and the gamma-ray measurements.

The author also made use of the radium content of the monazite sand and the concentrate to obtain the percentage of recovery of mesothorium in the crude concentrate.

After the dry concentrate was carefully composited, it was weighed and the following quantitative determinations were made:

1. The percentage of barium suphate in the crude concentrate; the amount of barium chloride added to the ore being known, the recovery of barium could be calculated. Assuming that the mesothorium accompanied the barium in the plant process, the recovery of barium represented the recovery of mesothorium.

2. The gamma-ray activity of the crude concentrate in terms of radium was determined by sealing up duplicate samples of 50 grams each, and after the lapse of a month comparing their gamma-ray activity with 50-gram samples of barium sulphate of known radium content sealed in glass tubes of the same dimensions. The radium content of the samples of barium sulphate used as standards was carefully determined by the emanation method, and was so adjusted that the gamma activity did not differ very much from that of the mesothorium concentrates. The comparisons of gamma-ray activity were made with a Wulf quartz fiber electrometer (39) of small electrostatic capacity (40), the brass ionization chamber being screened by a sheet of lead 3.3 mm. thick.

3. The radium content of the monazite sand was determined on 10-gram samples by the emanation method, employing concentrated sulphuric acid to decompose the ore. The radium emanation was collected quantitatively over mercury in a special form of apparatus described by Underwood and Schlundt (41). This apparatus was also used in most of the determinations of radium in samples of the crude concentrates. The values marked (*a*) in the following table were determined from samples of the purified concentrate by fusing with mixed carbonates and then following the method of Lind (43), for the determination of radium. As radium and mesothorium are isotopic elements, calculations based on the recovery of radium are values for the recovery of mesothorium.

4. Finally, determinations were made of the losses of mesothorium in the various liquors and products separated in the plant process before the crude concentrate was recovered. These losses were based on the radium content of samples of eight different liquors, and in

the coarse unattacked ingredients (tailings) of the ore that remained in the first tank after the phosphates had been slimed off.

The experimental data are given in condensed form in Table 7.

TABLE 7.—*Experimental data on ratio, MsTh: Th.*

Item.	Run No. 1	Run No. 2.
Quantity of monazite sand taken, pounds	10,800	11,400
Thorium element present, per cent	5.70	5.74
Total thorium in charge, grams	2.792×10^{5}	2.968×10^{5}
Radium per gram monazite, grams	7.16×10^{-10}	7.912×10^{-10}
Total radium in ore charge, mg	3.507	4.092
Dry weight of crude concentrate, pounds	62	39.21
Total barium added to ore charge expressed as $BaSO_4$, kg	22.31	12.121
Barium sulphate in crude concentrate, per cent	52.2	46.91
Barium recovered in crude concentrate, kg	14.68	8.343
Barium recovered, per cent	65.8	68.8
Radium content of crude concentrate, per gram	84.9×10^{-9}	141.7×10^{-9}
Do. [a]	79.9×10^{-9}	146.6×10^{-9}
Total radium in concentrate, mg	2.39	2.520
Do. [a]	2.247	2.607
Recovery of radium, per cent	68.1	61.6
Do. [a]	64.1	63.7
Combined radium losses in liquors, per cent	.....	24.73
Radium loss in sand residue (tailings), per cent	8.1	5.85
Total radium losses, per cent	.....	30.58
Radium recovery based upon losses, per cent	.....	69.42
Gamma-ray activity per gram concentrate, grams Ra	520×10^{-9}	879×10^{-9}
Gamma-ray activity ThD in concentrate, per cent	8.0	7.8
Gamma-ray activity of MsTh and Ra per gram, Ra	478×10^{-9}	810×10^{-9}
Total gamma-ray activity of MsTh and Ra in ore:		
(1) On basis of barium recovery, mg. Ra	20.46	20.95
(2) On basis of radium recovery, mg. Ra	20.34	23.00
(3) On basis of radium losses, mg. Ra	.....	20.75
Average, mg. Ra	20.40	21.57
Deducting radium content of ore, mg. Ra	3.51	4.09
Leaving mesothorium content of ore, mg. Ra	16.89	17.48
Ratio, MsTh:Th	6.05×10^{-3}	5.89×10^{-3}
Ratio, Th:MsTh	16.5×10^{6}	[b] 17.0×10^{6}
Total gamma activity due to radium, per cent	17.2	18.9

[a] Determined from samples of purified concentrate by fusing with mixed carbonates and following Lind's method for radium.

[b] Corrected for the difference in absorption of the gamma rays of radium C and mesothorium 2, the ratio becomes approximately 13.6×10^{6}.

The percentage of the gamma activity due to radium in the final high grade mesothorium recovered from the crude concentrate of run No. 2, and having an activity weight for weight very close to that of the radium standard containing 65 per cent of anhydrous radium bromide, was determined by the emanation method and found to be 16.8 per cent, a value in fair agreement with the percentage of gamma activity 18.9 per cent for radium in the monazite sand.

The author's experiments give a value of 16.7×10^{6} grams of thorium in equilibrium in a mineral with 1 gram of mesothorium expressed in terms of the gamma activity of radium. It is also seen that the mesothorium approximates four and a half times the radium content of these Brazilian monazites, and that a ton falls a little short of containing 3 mg. (See Table 2, page 11.)

The relatively low recovery of mesothorium, 65 to 70 per cent, in these plant runs probably should be attributed mainly to mechanical losses of barium sulphate in the copious wash liquors used in the recovery of thorium. The results thus show what fraction

of the mesothorium may be recovered in the plant process for the extraction of thoria from monazite, before the process has been modified materially to increase the yield of mesothorium.

EXTRACTION OF MESOTHORIUM FROM MONAZITE SAND.

For several years after Hahn's discovery (44) of mesothorium in 1907, its method of extraction was kept a technical secret. But when Soddy (45) and Marckwald (46) a few years later independently established the chemical identity of mesothorium with radium, the trade secret vanished. Evidently the well known methods of extracting radium thereby became standard procedures for the production of mesothorium. Though the chemistry of mesothorium and the methods of preparation are thus clearly defined, its production presents many problems for investigation. In the extraction of radium from carnotite ores, for example, the chemical treatment of the ore aims at the separation of radium as the primary product. The recovery of mesothorium, on the other hand, consists in conserving a secondary product obtained in the manufacture of thorium nitrate from monazite sand. The investigations presented in this paper represent a modest contribution to some of the problems that arise in this connection. This study included (1) a determination of the quantity of mesothorium associated with thorium in Brazilian monazite sand; (2) the percentage recovery of mesothorium in the plant process employed by the extraction of thorium; (3) the losses of mesothorium in different stages of the process; (4) experiments on refining the crude concentrate of barium sulphate bearing the mesothorium; (5) methods of analysis, chemical and radioactive, of the materials and products employed; and (6) laboratory experiments involving modifications of the plant process to increase the yields of mesothorium.

LABORATORY EXPERIMENTS ON THE EXTRACTION OF MESOTHORIUM FROM MONAZITE SAND.

In his paper on the chemistry of mesothorium, Soddy (45) described several experiments on the separation of mesothorium from monazite sand. In one experiment, 800 grams of monazite sand were decomposed by heating with twice its weight of concentrated sulphuric acid to which about 0.1 per cent of barium carbonate had been added before heating. The product was stirred with cold water, and the muddy liquor obtained was decanted from the unattacked ingredients in the sand. The sediment obtained from the muddy solution contained practically all the mesothorium and radium in the monazite. The sediment from 800 grams of monazite weighed 14.5 grams and contained practically the whole of the

material. The unattacked sand retained 8 per cent of the material. A further precipitation of 1.6 grams of barium sulphate formed in the clear monazite solution possessed a small initial activity, due to regenerated thorium X only, which decayed almost completely in the course of a month. Soddy estimated that less than 5 per cent of the mesothorium was present in the solution. The presence of thorium X in the precipitate of barium sulphate and the absence of mesothorium are regarded as clear evidence that practically the whole of the mesothorium can be separated from monazite by this method. Measurements were made by the gamma-ray method both of the original material and of the sediments. The gamma activity of the main sediment fell to 57 per cent of its maximum value in the course of a month, as the effect of the decay of thorium X exceeded the increase due to the generation of radium C.

Soddy's procedure for extracting mesothorium was repeated in several experiments with 500 grams of monazite sand containing 6.54 per cent of thorium oxide. One gram of barium chloride was added to the samples, before heating the sand with twice its weight of concentrated sulphuric acid. Four per cent of the acid boiled off during cooking. The resulting paste after cooling was stirred up with 8 liters of cold water, and the muddy liquor slimed off. The unattacked sand was stirred up with another liter of water, and this liquor was decanted off and combined with the larger volume, thus making a solution containing about 10 per cent sulphuric acid. The sediment from this solution had a dry weight of 6.2 grams, the unattacked sand 46.2 grams. In the course of several days the acid liquor gradually gelatinized on account of the partial separation of thorium as phosphate.

As the measuring instruments were not sensitive enough for accurate measurements of the gamma radiation of monazite sand, the recovery of mesothorium and the losses were obtained by making radium determinations in the monazite, the sediment bearing the mesothorium and radium, the unattacked sand, and the liquors. The radium determinations were made by the emanation method. From the sand, the unattacked residue, and the concentrate bearing the mesothorium and radium, the emanation was separated by boiling suitable samples of these materials with concentrated sulphuric acid, collecting the emanation thus liberated quantitatively, and measuring it electroscopically in calibrated air-tight electroscopes (41).

As the liquors coagulate upon boiling owing to the separation of thorium phosphate, it was necessary, in order to hold the thorium in solution, to acidify the liquors more; for this purpose concentrated hydrochloric acid was used. The emanation could then be separated quantitatively by boiling, as in the quantitative determination of radium emanation present in natural waters.

The radium content of the sample of monazite sand used, containing 6.54 per cent thorium oxide, was found to be 7.98×10^{-10} grams per gram when the determinations were made by decomposing the sand with concentrate sulphuric acid, and 8.21×10^{-10} grains when the radium determinations were made by fusion of the finely ground samples to which a little barium salt had been added with mixed alkali carbonates followed by estimation of radium directly in the refined barium sulphate.

The radium retained in the unattacked sands was found to be 6.5 per cent by the sulphuric acid method, and 7.4 per cent by the method involving fusion with mixed carbonates of sodium and potassium. These results confirm the loss of about 8 per cent reported by Soddy.

In the liquors were found 5.6 per cent of the radium, making a total loss of about 12 per cent. In the radium-mesothorium bearing concentrate, 84 per cent of the radium in the ore charge was recovered, leaving 4 per cent unaccounted for.

PLANT EXPERIMENTS ON THE EXTRACTION OF MESOTHORIUM FROM BRAZILIAN MONAZITE.

No experiments were conducted on a plant scale to ascertain whether corresponding recoveries of mesothorium could be duplicated. As already stated, in the plant runs the mesothorium-bearing concentrate was separated at a later stage of operation. The intermediate stages include several treatments where rather large volumes of liquor are decanted off, therefore it is not surprising that the recovery of mesothorium falls to 65 per cent as a result of mechanical losses of barium sulphate in these operations. The successive treatments of crude thorium phosphate eliminate nearly all of the phosphoric acid, and when the thorium chloride solution is finally obtained, a black slimy residue remains which bears the active barium sulphate.

After the residue had been washed twice with water by decantation, it was transferred to a stoneware suction filter and given another washing or two with hot water. Before analytical work on it was begun the residue was dried for several days in steam kettles or on hot plates. At this stage the residue consisted of small, grayish black lumps having the texture of rather low-grade graphite. This product was then pulverized to pass through a 20-mesh sieve by means of a disk pulverizer, after which it was carefully composited by quartering. The product is termed in this paper the crude concentrate of mesothorium. Duplicate samples of 500 grams each were set aside for analytical determinations of barium, lead, and radium, and for gamma-ray measurements. These samples also served in part for the laboratory experiments on the preparation of refined concentrates, which are described in a later section.

From the data summarized in Table 7 (p. 19), it was concluded that the addition of 1 pound of barium chloride to 400 pounds of ore instead of 1 to 200 pounds does not reduce the percentage recovery of mesothorium in the crude concentrate. In later runs, it was found that the addition of one-fifth of 1 per cent of barium chloride crystals to the ore charge was sufficient to protect the mesothorium. The crude concentrate obtained when the smaller amount of barium was added, generally contained a little more than 1 milligram of gamma-ray activity per kilogram of weight.

The factor for the conversion of pure barium chloride, $BaCl_2$ $2H_2O$ into barium sulphate is 0.955. In the first plant run, the crystals of barium chloride added gave 91.15 per cent of their weight of barium sulphate. In the second run, the factor was 0.9376. These factors were used in calculating the quantities of barium sulphate that resulted from the quantities of chloride added in the respective runs.

A complete analysis of the crude concentrates was not attempted. The analytical data obtained clearly show that the concentrates are complex mixtures, and in comparison with the "First sulphates" (47) of radium-barium separated in the recovery of radium from carnotite ores, they are of low grade in barium content. By qualitative tests it was found that the crude concentrates were practically free from silica, but that 1 to 2 per cent of phosphoric acid was still present. A small amount of thorium was also retained; lead was also present—some of it soluble and some insoluble in water. The source of the graphite and amorphous carbon present Mr. Gulbrandsen traced to the iron pots in which the sand was cooked with sulphuric acid. In the early plant runs the quantity of carbon present in the crude concentrate was more than was required to reduce the barium sulphate to sulphide. Some lead chloride could be extracted from the concentrate by digestion with hot water. By far the larger proportion of the lead was present as sulphate. Its amount varied considerably in different concentrates. From the concentrate obtained in plant run No. 2, nearly 5 per cent of lead chloride was extracted by successive treatments with hot water. After the removal of the lead chloride from this concentrate, a determination of lead showed that an additional 15 per cent of lead sulphate remained in the concentrate. The percentage of barium sulphate present in four different lots of concentrate analyzed ranged from 52 per cent in run No. 1 to 37 per cent in one of the later plant runs.

By making radium determinations on composites of the different wash liquors it was found that the radium losses in the acid solutions amounted to 34.6 per cent in run No. 1 and only 20.2 per cent in run No. 2. No explanation for this marked difference was evident. The

losses in the alkaline liquors were relatively low—5.7 per cent in No. 1 and 4.5 per cent in No. 2.

Fully two-thirds of the combined losses in the liquors was confined to one of the acid liquors. Though the investigators were at first inclined to attribute the major portion of this loss to chemical action, later, after examination of the sediment in this liquor, it was concluded that the loss was almost entirely mechanical, barium sulphate having been carried over in the wash liquors when they were siphoned off. The loss of values in the unattacked sands appears to correspond to the weight. In the first run the tailings constituted 9.4 per cent of the monazite sand treated, and the radium found was 8.3 per cent. In the second run the unattacked sands constituted 6.1 per cent of the weight of the ore, and the percentage of radium found was 5.85 per cent.

In conducting the analytical work, determinations were generally made in duplicate or triplicate by at least two methods. In the estimation of radium, for example, in monazite, and the concentrates, the two methods have already been outlined. By following this plan throughout the investigation it was learned that several of the methods of analysis required modification.

The radium determinations in monazite sand gave values 5 per cent higher when the ore was decomposed by fusion with mixed carbonates instead of sulphuric acid, therefore it was concluded that the residue that was unattacked by sulphuric acid held materials containing radium. This conclusion found confirmation in the radium determinations made on the unattacked sands by both methods. When the emanation was separated directly by boiling with concentrate sulphuric acid, the values were scarcely a third as high as those obtained by first decomposing the tailings by fusion with mixed alkali carbonates.

DETERMINATIONS OF LEAD AND BARIUM IN THE CONCENTRATE.

In the first method of analysis the lead and barium were extracted with concentrated sulphuric acid, and the recovered sulphates were then refined by fusion with mixed alkali carbonate, and finally after separation were precipitated as sulphates. As the percentages of lead and barium found in this method stand in close agreement with the results obtained by direct fusion of the concentrate with mixed alkali carbonates, confidence was gained in the method of determining radium in the concentrate, when the emanation is separated by boiling samples with concentrated sulphuric acid. The fact that lead and barium can be extracted quantitatively from the crude concentrate with concentrated sulphuric acid also suggests a possible method of refining this product on a commerical scale.

In the analytical determinations 5-gram samples of the concentrate were boiled for 10 minutes with 120 c. c. of chemically pure sulphuric acid. After cooling somewhat, the insoluble residue was filtered off on a Gooch crucible with asbestos mat, and washed twice with hot concentrate acid. From the filtrate, lead and barium were precipitated by dilution with two to three liters of water. The recovered sulphates were then refined by fusion with mixed carbonates and the washed carbonates were converted into chlorides. To separate the lead the filtrate was made barely alkaline with ammonia, and then saturated with hydrogen sulphide. In the filtrate barium was precipitated as sulphate; lead was also estimated as sulphate in the solution obtained by dissolving the precipitate of lead sulphide in dilute nitric acid.

In the other method, 5-gram samples of the crude concentrate were fused directly with mixed carbonates in nickel crucibles. An insoluble residue of nearly 10 per cent generally remained when the washed carbonates were treated with dilute hydrochloric acid. A second and third fusion, however, did not yield additional barium or lead. In the concentrate from run No. 2 the writer found 46.56 per cent of barium sulphate by extraction with sulphuric acid and 47.26 per cent by direct fusion with mixed carbonates. In run No. 2 the lead content of concentrate was estimated as at least 21 per cent sulphate. This high percentage of lead sulphate in concentrate No. 2 explains an observation made subsequently in connection with experiments on refining the crude concentrate. When heated, much sulphur dioxide is liberated at about 600° C., probably as the result of the interaction of lead sulphide formed by the reduction of some of the lead sulphate by carbon, with unreduced lead sulphate.

REFINING OF MESOTHORIUM IN THE CRUDE CONCENTRATE.

The method finally employed for extracting the barium in the two batches of crude concentrate that was obtained in experimental runs 1 and 2, and for obtaining it in soluble form followed closely the process used in refining the "first sulphates" (47), produced in the extraction of radium from carnotite ores. The barium sulphate carrying the radium at a concentration of about 1 mg. kilo was intimately mixed with charcoal and was then reduced to sulphide at about 1000° C. The reduced product when leached with hydrochloric acid gave a solution of barium chloride, ready for further concentration of mesothorium by fractional crystallization.

Before adopting the direct reduction method, a number of laboratory experiments were conducted with 5, 10, 50, and 100-gram samples of the crude concentrates of mesothorium-barium with a view to securing data on other methods of possible practical value.

In outlining the methods of analysis attention was directed to the quantitative extraction of barium from the concentrate by digesting it with a large excess of concentrate sulphuric acid. In order to insure the barium being completely dissolved in the concentrate it must be boiled with at least six times its weight of acid. About 40 per cent of the material remains unattacked. When the black residue is filtered off on a suction filter fitted with asbestos mat and washed with two portions of hot concentrate sulphuric acid, fully 95 per cent of the barium may be recovered upon diluting the acid liquor with 10 to 15 times its volume of water. The partly refined sulphate thus obtained may be converted almost quantitatively into soluble form by one of three methods: (1) Reduction to sulphide at high temperatures by carbon; (2) conversion into carbonates by fusion in iron kettles with a mixture of sodium hydroxide, 1 part, to soda ash, 2 to 3 parts, leaching of the fused mass, washing free from sulphates, and conversion of the insoluble carbonates into chlorides—recoveries running as high as 97 per cent were obtained by this method; (3) prolonged boiling of the refined sulphates with a concentrated solution of sodium carbonate about four times in excess of the sulphates present. With constant stirring by means of a mechanical stirrer during the digestion period, conversions as high as 92 per cent were obtained. Methods 2 and 3 can be applied directly to the crude concentrate with equally good results. More than 20 preliminary experiments of this character were conducted with 50-gram samples of concentrate before the decision was reached to treat the main bulk of the concentrate by direct reduction with carbon as the first step in refining.

In the early reduction experiments, 500-gram charges were carried through and the amount of soluble barium determined. At first enough powdered charcoal or lampblack was mixed with the crude concentrate to reduce all of the barium and lead sulphates. In the course of the experiments, it was soon noted that the residue remaining after the reduced product had been leached with hydrochloric acid was nearly as bulky as the original charge. Furthermore, some experiments to determine the loss on ignition revealed the reduction of a large fraction of the sulphates. In short, it soon became evident that the admixture of graphite and amorphous carbon present in the crude concentrate was more than enough to reduce the sulphates completely. The concentrates from the two experimental runs were reduced in the technological laboratory of the United States Bureau of Mines at Golden, Colo., and later, after it was found that the concentration of mesothorium by fractional crystallization of the chlorides and bromides proceeded normally, two other batches of concentrates weighing, respectively, 349 and 745 pounds[a]

[a] Experimental data are given for a part of this concentrate, 179.3 kg., in Table 8, page 27.

were given this treatment in the plant of the Welsbach Co. The reductions were carried out in graphite crucibles with 30-pound charges heated 4 to 5 hours at 1100° C. and sometimes even higher. The recovery of values and the losses in the various products were investigated throughout the experiments by two distinct methods of analysis: The chemical method involving determinations of barium, and the radioactive method, embracing comparisons of gamma-ray activities and determination of radium by the emanation method. The more important experimental data are summarized in Table 8.

TABLE 8.—*Refining of crude concentrates of mesothorium.*

Item.	Concentrate expt. run No. 1.	Concentrate expt. run No. 2.	Plant concentrate No. 1.	Plant concentrate No. 2.
Dry weight, kg	26.08	16.77	158.5	179.3
Loss of weight during reduction, per cent	24.4	41	30.1	27.7
Barium sulphate content, per cent	52.2	46.91	[a] 44.7	[c] 37.82
Total $BaSO_4$ in concentrate, kg	13.61	7.867	70.85	67.81
Radium per gram concentrate, grams	$82.4\times10^{-}$	144.2×10^{-9}	181×10^{-9}	172×10^{-9}
Total radium in concentrate, mg	2 [illegible]	2.418	28.69	30.84
Weight of insoluble residue, kg	6.53	3.069	[b] 64.3	48.59
Barium sulphate content of residue, per cent	7.12	5.9	8.83	[c] 1.57
Total $BaSO_4$ in residue, kg	.46	.181	5.678	.763
Part of barium in residue, per cent	3.4	2.3	8.01	1.12
Ra in residue per gram, grams	.....	.....	62.1×10^{-9}	6.4×10^{-9}
Total Ra left in residue, mg	.....	.....	3.99	0.311
Ra loss, per cent	.....	.....	13.9	1.01
Gamma activity of $BaCl_2$, mg. per kilo	1.02	1.79	2.77	2.58
Total MsTh and Ra in $BaCl_2$, mg	10.2	12.1	152.2	156.2
Radium in chloride, mg	.....	.....	24.8	30.0
MsTh in choride, mg	.....	.....	127.4	126.2
Activty due to radium, per cent	.....	.....	16.3	19.2

[a] Anaysis by Mr. Super.
[b] This weight includes, in addition to the residue insoluble in hydrochloric acid, the precipitate obtained in the filtrate made slightly akaline with ammonia.
[c] Anaysis by Mr. Terry.

Before outlining further the refining process followed in obtaining the data presented in Table 8, a few words on the sequence of the experiments and on the radium losses in the insoluble residue that remains after reduction is leached with hydrochloric acid will throw light on the comparatively high losses of radium, 14 per cent, which were permitted in refining the first batch of plant concentrate, weighing 158.5 kg. It will be noted that the radium content of the residue remaining insoluble in the hydrochloric acid was not determined in working with the concentrates of experimental runs 1 and 2, which were refined in Golden. It was assumed that the loss of radium corresponded to the loss of barium, which averaged about 3 per cent. By extending the time of reduction and finally by raising the temperature to 1,200° C., successive trials with 500-gram charges showed a steady decrease of barium losses in the insoluble residue, until toward the close of the experiments it dropped to 1.4 per cent. The actual recovery of mesothorium in the chlorides, however, showed a loss of about 10 per cent. This discrepancy was not

noted at the time, as those performing the tests were busily engaged on the further concentration of mesothorium by fractional crystallization. Later, after nearly all of the first lot of concentrate in the plant weighing 158.5 kg. had been reduced and the barium had been converted into chlorides, time was found to make radium determinations. It was then discovered that in departing hastily for a time from the good rule of checking analytical results during the experimental stage of the investigation by an independent method, a serious loss of values had not been detected. This discrepancy is considered in more detail below.

The concentrate after reduction is not very compact and does not require to be pulverized for ready conversion into chloride. The treatment of the reduced product with hydrochloric acid is conveniently conducted in stoneware pots. As considerable frothing takes place, the sulphides must be added cautiously and the solution stirred continuously. Chemically pure acid of 10 per cent strength was used, but not in large excess. When the liberation of hydrogen sulphide had about ceased, the liquor was heated by steam. The solution was then made slightly alkaline with ammonia and the liquor was again boiled to promote settling of the precipitate. The addition of ammonia precipitates lead, iron, and other heavy metals and gives a residue which filters off quickly, the filtrate being clear. As the insoluble residue and precipitate are bulky, a large stoneware suction filter was used, fitted with paper that was covered with canvass.

The residue was given four to five washings with hot water. The first and second washes were combined with the first filtrate, and the liquor was sent to the evaporator to be concentrated. The other wash liquors were combined and used as first and second wash waters for the next batch of concentrate treated. With each addition of wash water the entire product on the filter was worked up into a slip. After drying, the residue was composited and samples were reserved for the determination of barium and radium.

The residue insoluble in hydrochloric acid averaged about 38 per cent by weight of the reduced product from plant concentrate No. 1, plus the precipitate produced by ammonia, the total insoluble became nearly 58 per cent. In terms of the original, the unreduced concentrate, it may be seen that the residue insoluble in hydrochloric acid plus the precipitate produced by ammonia amounted to 40 per cent.

In refining the plant concentrate No. 1, it should be noted that the barium and radium determinations were not made directly on the residue unattacked by hydrochloric acid, but on the product including in addition the precipitate formed by ammonia. Inas-

much as radium determinations were not made at first, and as the barium determinations averaged 2.8 per cent, the result was considered a satisfactory recovery at this stage. Later, when it was possible to make radium determinations, one of these residues unexpectedly indicated a loss of 12.8 per cent. The analytical method for the determination of barium and its separation from lead were then modified, with the result that on the average 8.83 per cent of the barium in the reduced concentrate was left in the residues. The radium determinations, however, gave higher values, averaging 13.9 per cent, the value given in Table 8.

That this excessive loss of mesothorium in the residues was not due to incomplete reduction of the sulphates was established by determining directly the radium and barium content of the residues insoluble in hydrochloric acid before the acid was neutralized with ammonia. The radium and barium determinations then stood in good agreement, as the data for plant concentrate No. 2 clearly show. The addition of ammonia caused a precipitation of some barium leached from the sulphides. Further investigation revealed the presence of a small amount of phosphoric acid in the crude concentrate. Evidently, when the chloride liquor was made alkaline, some barium was precipitated as phosphate. A quantitative determination of phosphoric acid, however, gave a value equivalent to barely one-third of the additional quantity of barium precipitated by ammonia. Moreover, it will be noted that the loss of values based upon the radium determinations greatly exceeded the percentage of barium left in the residue, including the precipitate with ammonia. Evidently the treatment with ammonia precipitated some of the radium without the corresponding quantity of barium. Unless it is assumed that the solution contained some other element which acted like barium in the separation of radium, this result indicates that the fractional precipitation of barium as phosphate, when the chloride was made alkaline with ammonia, produced an enrichment of radium similar to the process of fractional crystallization.

When the foregoing relations were recognized, neutralization with ammonia was, of course, discontinued. Although the insoluble residue to be filtered off from the acid liquor bulked scarcely more than half that in the alkaline solution, the finely divided graphite soon clogged the filters. This filtration problem was solved by Mr. J. G. Buckley, of the research staff of the Welsbach Co., who added a fair proportion of paper pulp to the residue, with the result that filtration became fairly rapid.

The relatively large amount of lead chloride crystals that separated out on cooling the acid chloride liquor, introduced another difficulty. No ready method was known of separating these crystals

before filtering off the insoluble residue, therefore the acid liquor was filtered while hot. Upon cooling, most of the lead chloride crystallized out and the clear liquor could be decanted. The lead chloride remaining in solution tended to accumulate with the mesothorium during the fractional crystallization. A large part of the lead was then removed, first, after three or four fractionations of the chlorides, later, after the chlorides were converted into bromides, and finally once or twice more during the fractionation of the bromides.

The first series of barium determinations in the plant on the insoluble residue from plant concentrate No. 1 ran so far too low, that the analytical procedure was obviously faulty, notwithstanding the fact that duplicates gave very good checks. The regular program of work did not afford time for a full investigation of this problem. The higher values recorded in Table 8 were obtained by the following method: The weighed samples were first freed from carbon by ignition. The roasted product was then fused with mixed carbonates of sodium and potassium. The insoluble carbonates were washed free from sulphates and then dissolved in hydrochloric acid. Lead and other heavy metals were removed from the filtrate by saturating with hydrogen sulphide after it had been made slightly alkaline with ammonia. After acidifying the filtrate, barium was precipitated as sulphate. A second fusion of the residue insoluble in hydrochloric acid with mixed carbonates yielded only a mere trace of barium. The hydrogen sulphide precipitate was found to be free from barium. Observations pointed to the large amount of carbon still present in the insoluble residue, because of its powerful reducing action in fusion, as the disturbing factor in the ordinary analytical procedure. The barium values recorded were confirmed by extracting the barium with concentrated sulphuric acid as described on pages 24 to 25.

When the third lot of plant concentrate came through for treatment the reduction was not a success. In some runs only 60 per cent of the barium could be extracted from the reduced sulphides with hydrochloric acid, and rarely were the recoveries of barium as high as 80 per cent. This unexpected result may perhaps be attributed to a change in the composition of the crude concentrate due to some modification of the plant process of extracting thorium from monazite sand. The concentrate contained free silica, and this possibly reacted at the high temperature of reduction with barium to form compounds that remained unattacked by hydrochloric acid. Mr. S. Gulbrandsen, assistant chemist of the Welsbach Co., has worked out a method of treating the crude concentrate with soda ash, which has proved successful for the conversion of barium into chloride. The details of this method have not been released for publication.

CONCENTRATION OF MESOTHORIUM BY FRACTIONAL CRYSTALLIZATION

THEORETICAL DISCUSSION.

Mesothorium and radium having identical chemical properties, the concentration of mesothorium or of mixtures of mesothorium and radium by fractional crystallization of the barium solutions, is in practically all respects the same process as that of concentrating radium. In chloride or bromide solutions the mesothorium continues to be enriched in the crystal fractions, and impoverished in the successive mother liquors. The chlorides and bromides of mesothorium and radium are less soluble than the barium salts, a relation that favors an enrichment of mesothorium and radium in the crystals. On the other hand, the solubility of the hydroxides of the alkaline earth metals increases with increase of atomic weight, and in the fractional separation of the hydroxides mesothorium enriches in the solution (49).

The factor of concentration or enrichment, also called the crystallization factor, in each step of the chloride fractionation is about 1.5 to 1.6 (47), and from 2 to 2.2 in acid bromide systems. The enrichment is considered more favorable in acid than in neutral solutions. It is evident, however, that the crystallization factor depends on the fraction of salt that crystallizes out. The factors given refer to the conditions followed in the practice of evaporating the solution to the point where approximately half of the barium in solution separates on cooling; the evaporation is regulated by noting when a stream of air blown on the surface of the hot solution just causes the formation of crystals. The fraction of crystals that separates under this condition, however, varies more or less with the acidity of the solution.

The terms "crystallization factor," "concentration factor," "factor or enrichment," " fractionation coefficient," seem to be used synonymously in published accounts of the refining of radium, but not always with the same meaning. Evidently these terms always refer to a ratio, but the ratio may be expressed in several related ways, as (1) the concentration of mesothorium in the crystals separated to the concentration in the original crystals used in preparing the solution—concentrations being given as milligrams of mesothorium, (expressed in terms of radium), per gram or kilogram of anhydrous crystals, $(C_c : C_o)$; (2) total mesothorium in crystals to total mesothorium in mother liquors, $(Q_c : Q_l)$; (3) concentration of mesothorium in crystals separated to concentration in crystals from mother liquor, where the ratio is used in the sense of a partition or distribution coefficient, $(C_c : C_l)$.

Throughout this the term crystallization factor is given the first meaning. This factor serves directly in computing the mesothorium content of the head crystals in fractionations, as this factor raised to the nth power—n being the number of crystallizations—gives the desired multiplier. In this connection it is of interest to note that the crystallization factor by definition 1 must be less than 2, when the solution is concentrated enough to crystallize out 50 per cent of the solute. For assuming the factor as 2, and one-half the solute as crystals, it follows that all of the mesothorium appears in the crystals—a result that is contrary to experiment.

A few examples will show how the three factors are related and applied. Assume the crystallization factor 2.0, when 42 per cent of the barium bromide in a given solution crystallizes out. This relation is based upon the investigation of Nierman (48) conducted in the chemical laboratory of the University of Missouri during the session 1918–19.

To make the matter concrete, consider a stock solution of bromide liquor containing 80 milligrams of mesothorium per kilogram. The problem is (1) to deduce the quantities of salt and the mesothorium content in the crystals and the mother liquors obtained in each dish in the successive series of fractionations, and (2) to work out from these results a crystallizing system with the minimum number of dishes or transfers. The concentration of mesothorium in the bromide of the mother liquor of course should be approximately the same as in the crystals with which it is combined for further fractionation.

The solution of the problem is shown by figure 2. Besides the number of the dish, each circle in the diagram contains the weight in grams of salt in the dish and the concentration of mesothorium. The amount of mesothorium in each dish stands to the right on the plus side and to the left on the minus side. The crystals pass up in successive series, whereas the liquors pass toward the minus side, and crystals and liquors of the same concentration always meet and will continue to do so unless somewhat disturbed by the introduction of fresh stock liquor, as shown in zero dish of series 4. As long as the fractions of crystals that are separated remain constant, liquors and crystals of the same concentration will always meet when the simple plan of transfer of the diagram is followed.

As 42 per cent of the salt crystallizes, 420 grams of crystals will be obtained upon the first fractionation whose concentration is 160 milligrams per kilogram, making the total mesothorium in the crystals 67.2 milligrams or 84 per cent, and 16 per cent of 80, or 12.8 milligrams of mesothorium in mother liquor, which contains 580 grams of salt. Hence the concentration of mesothorium in the salt remaining in solution is $12.8 \div .580 = 22.1$ milligrams per kilogram of anhydrous

bromide. As the crystals contain 160 milligrams mesothorium per kilogram, the ratio $\frac{160}{22.1}=7.24$, shows how many times more concentrated the mesothorium is in the crystals separated than in the salt of the mother liquor. Another relation is of interest. As 84 per cent of the mesothorium is in the crystals and 16 per cent in the mother liquor, it is seen that in the parting 5.25 times as much mesothorium appears in the crystals as remains in the mother liquors.

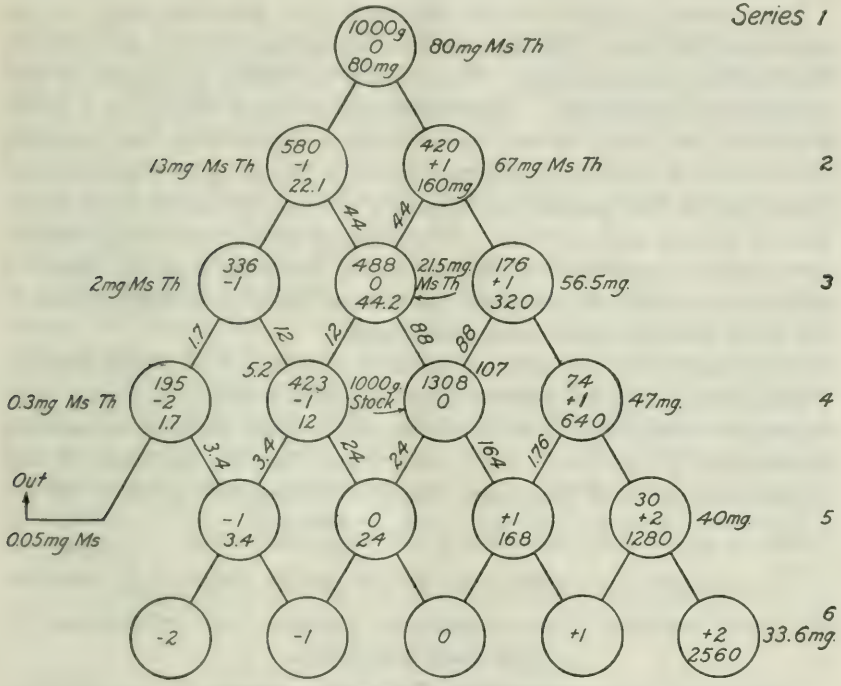


FIGURE 2.—Bromide crystallizing system.

This example supplies the fundamental constants to be applied to each crystallization throughout the entire fractionation process.

Distribution of salt in process of concentration.

Salt as crystals, per cent, p	0.42
Salt in mother liquors, per cent	.58
Corresponding crystallization factor, c	2.0
MsTh in crystals, per cent, pc	.84
MsTh in mother liquor, per cent, $1-pc$	.16

Concentration ratio of MsTh in crystals to liquors 7.24 (factor, definition 3). Finally the crystals contain 5.2 times as much MsTh as remains in the liquor (factor, definition 2).

The following calculations for dish plus 1, after the second crystallization, will show the system of checks employed.

Crystals: Weight $0.42\times420=176$ grams; MsTh conc., $C_c=320$ mg. per kg. Total MsTh$=0.84\times67.2=56.5$; check, $0.176\times320=56.5$ mg.

Mother liquor: Weight of salt, $0.58\times420=244$ grams,

MsTh total$=0.16\times67.2=10.7$; check, $67.2-56.5=10.7$.

MsTh concentration, $C_1=\frac{10.7}{0.244}=44$ mg. per kg.

MsTh concentration, C_1 check, $\frac{320}{7.24}=44$ mg. per kg.

The results of similar calculations for other dishes are given in the diagram.

The underlying idea of the diagram is to have the steps in the concentration from dish to dish in each series as great as possible, 7.24 for the example cited. The number of dishes in a series is thus reduced to a minimum. Additional intermediate dishes in a series as Scholl (56) describes may be at times a convenience, but the extra dishes are not necessary and merely make the steps in concentration from dish to dish smaller, and greatly increase the number of transfers of liquors and crystals. In operating any crystallizing system, care must be exercised in adding stock liquor to a point where it will be combined with crystals (or mother liquor) of approximately the same concentration in mesothorium.

Supposing that a chloride system is operated with stock solution containing 1.8 mg. mesothorium per kg. of dry salt, how many crystallizations will have to be made to obtain head crystals containing 50 mg. MsTh per kilo? If it is assumed that 45 per cent of salt crystallizes out each time, and that the corresponding factor of enrichment is 1.6, then the relation $1.6^n=\frac{50}{1.8}$, and $n=7$.

The examples here given typify the results obtained in practice.

RELATION BETWEEN CRYSTALLIZATION FACTOR AND PERCENTAGE OF CRYSTALS SEPARATED.

Nierman's (48) investigation of the concentration of mesothorium by fractional crystallizations of the bromides shows that the value of the factor of enrichment depends primarily upon the fractions of salt separated. A simple exponential relation appears to exist between the percentage of mesothorium in the crystals and the crystallization factor, as expressed in the equation: $Q_1=Q_oe^{-kp}$ where Q_1 represents the fraction of mesothorium remaining in the mother liquor, when Q_o, the amount of mesothorium in the solution to be crystallized, equals 1.00. The percentage of salt separated is given by p, and k is a constant expressing the continuous partition of mesothorium between mother liquor and crystals. The exponential relation indicates that the enrichment of mesothorium in the crystals is proportional always to the amount remaining in solution. Then since Q_c, the fraction of mesothorium in the crystals is $1-Q_1$, we have

$$Q_c=1-e^{-kp},$$

and $Q_c=ep$ (see p. 33).

The relation is not rigorous, for as Mr. S. Gulbrandsen kindly pointed out to the author, when p becomes 1, Q_c does not become 1 in $Q_c=1-e^{-kp}$ also, as it should for an exact relation. To derive the above relation one may write as a first approximation that dQ, the mesothorium separated during crystallization in the fraction dp of crystals, at the time the fraction Q of mesothorium still remains in solution, is kQdp. Integrating the equation dQ=kQdp gives the relation

$$Q_1=e^{kp}$$

To obtain a value for the constant k, the partition factor for fractionations with bromide solutions, one of Nierman's experimental values is introduced in the equation above. He found that approximately 12 per cent of the mesothorium remained in the mother liquor when 44 per cent of the salt crystallized out, and the liquor was drained off well from the crystals. Substituting these values in the above equation, the value of k is 4.8.

In preparing Table 9, the value 4.8 has been used for the constant k in the exponential formula. The first column headed Q gives the amount of mesothorium remaining in the mother liquor when the corresponding fraction of crystals in the second column was separated. In the third column are the values for the concentration factor, $C_c:C_o$ and in the last column the experimental values of Nierman, which were read off from a curve obtained by plotting crystallization factors on one axis and the corresponding percentages of crystals on the other axis of the ordinary system of rectangular coordinates.

TABLE 9.—*Crystallization factors in bromide fractionations.*

Q.	p, per cent.	Factor (calculated).	Factor (experimental).
0.619	10	3.91	.....
.383	20	3.08	3.05
.237	30	2.54	2.50
.147	40	2.13	2.11
.0907	50	1.82	1.805
.0561	60	1.57	1.57
.0346	70	1.38	1.36
.0215	80	1.22	1.21

Applying the simple exponential formula to chloride fractionations, one finds that the characteristic partition coefficient k has a value of approximately 3.0. This value is based on plant operations in which more or less mother liquor remains with the crystals in making transfers. The value 3.0 for k is based upon a factor of enrichment of 1.55 when 50 per cent of the chloride is separated as crystals. The actual partition coefficient for chloride probably has a somewhat higher value, and in acid solution the value seems to be a little higher still.

Doubtless certain experimental conditions, such as the rapidity of the separation of crystals and the degree of supersaturation, influence the value of enrichment. In the derivation of the simple exponential relation it has been assumed that the concentration of the barium bromide, though changing continuously during crystallization, remains fairly uniform in composition in different parts of the dish.

Nierman found that the crystallization factor remained constant up to a concentration of 2 mg. per gram, but the subsequent experiments described in this paper show that the factor remained fairly constant for higher concentrations. Even when the crystals that separate are as active, weight for weight, as pure radium bromide, no decline in the crystallization factor was observed.

DESCRIPTION OF EXPERIMENTS.

The next stage in the experiments for concentration of mesothorium included fractional crystallization of the chlorides and bromides of barium, radium, and mesothorium. The process of fractionation outlined was followed rather closely, particularly toward the close of the experiments. The type of apparatus described in Bulletin 104, Bureau of Mines (47), was used. No new retarding factors developed, nor was there gelatinous silicic acid in the author's chloride crystallizing system.

The initial concentration of mesothorium and radium in the chloride liquors obtained in the plant operations ranged from 2.2 to 2.9 mg. per kilo of anhydrous but impure barium chloride. After seven to eight fractionations, the chlorides attain a concentration of 50 to 60 mg. of mesothorium and radium per kilo when about 50 per cent of the barium was separated in the fractionations. This enrichment of mesothorium in the crystals corresponds to a factor of 1.5 to 1.6. At first the crystallizations were made in enamel-lined dishes from acid solutions containing 5 to 8 per cent of HCl, and about 60 per cent of the crystals were separated. The factor of enrichment was then only 1.4, and 10 series of fractionations were required to obtain head crystals containing 50 to 60 mg. of mesothorium per kilo. Later crystallizations were made from nearly neutral solutions in stoneware dishes concentrating to the point where approximately 50 per cent of crystals separate. For chlorides, the factor of enrichment appears to be 5 to 8 per cent higher for fairly acid than for neutral solutions.

When a concentration of 50 to 60 mg. of mesothorium per kilo of anhydrous crystals was reached, the chlorides were converted into bromides, the lead present being first removed. To this end the chloride solution was made slightly alkaline with ammonia, and

then was saturated with hydrogen sulphide. The precipitate of sulphides settled quickly, and was readily filtered off on a suction filter or large funnel. To the filtrate ammonia was added, and then to precipitate the barium completely as carbonate, either powdered chemically pure ammonium carbonate or a strong solution of ammonium carbonate. After settling overnight most of the supernatant liquid was poured off, and the rest went to a Buchner funnel, where it was filtered and was washed several times with hot water. The filtrates were returned to tanks in the plant in which thorium products were given caustic treatment.

The moist barium carbonate was next dissolved in 10 to 15 per cent chemically pure hydrobromic acid. From this point the fractionations were conducted in silica dishes. In five more fractionations the concentration of mesothorium went up 40 to 45 times in the head crystals when 40 to 45 per cent of the crystals were separated, which corresponded to a factor of enrichment of approximately 2.1.

When the bromide crystals attained an activity of 2 to 5 mg. per gram and weighed 1 to 5 grams, they were dried at 250° C., and sealed in a previously weighed tube of 3 to 5 mm. internal diameter, the date of sealing being noted. The total weight of the salt was determined by weighing the sealed tube and the piece detached in sealing. The salt was kept stored in the tube and after three days gamma-ray measurements were made against a radium standard at two or three intervals of a few days, or one final measurement was made after a month. By comparison of the activities with a curve showing the characteristic gain in activity of one of the tubed samples taken day by day against a radium standard, values may be obtained which were in good agreement with the values measured 30 to 40 days after sealing.

Up to this stage the fractionations were conducted in the plant. For the higher fractionations a comparatively small but well-equipped laboratory is required. It should be at least several hundred feet away from the laboratory for radioactive measurements, and preferably in a different building in order to guard against infecting the measurements laboratory or instruments with high-grade radioactive products.

After a sufficient number of the intermediate bromides had been accumulated, the tubes were opened, the salts combined, and then dissolved in a small volume of water for further purification and for separation of the radiothorium which had been produced after the bromides were sealed. After the solution was acidified with 1 to 2 c. c. of hydrobromic acid, it was filtered to remove a small insoluble residue, which was converted into soluble form by fusion with mixed carbonates of sodium and potassium and solution of the washed

carbonates in hydrobromic acid. A few milligrams of mesothorium was generally recovered from the insoluble residue to add to the main solution of bromides. The radiothorium present was separated with lead by adding 2 to 5 mg. of thorium bromide to the solution, making it faintly alkaline with ammonia and then passing in hydrogen sulphide to complete the precipitation of lead. The gamma activity of the product thus separated ranged from 2 to 10 mg., depending on the activity of the combined intermediate bromides and their age.

Before beginning fractionation of the bromides, it is well to evaporate to dryness, and smoke off the small amount of ammonium salts present, as the presence of even small quantities of impurities of this kind seems to affect unfavorably the texture of the crystal crop. No difficulty was experienced in obtaining compact crystals arranged in stellar groups when the ammonium salts were removed.

In the early tests the fractionations were made in an acid solution containing 5 to 10 per cent HBr. Later when Nierman (48) discovered that the factor of enrichment in neutral solution was practically as high as in acid solution, the crystallizations were conducted in nearly neutral solution, and thereby reduced materially the volumes of the solutions in the crystallizing system. Starting with 200 to 300 mg. of mesothorium, after six to eight series of fractionations, head crystals were obtained the gamma activity of which approached that of ordinary radium bromide containing 30 to 40 per cent radium element. Every time three more crystallizations were made another crop of high-grade head crystals came out.

After being thoroughly dried at 300° for at least an hour, the head crystals were sealed in small weighed tubes with a fine platinum wire sealed in at one end, and the weight of the anhydrous salt accurately determined, special care being exercised to exclude moisture by heating the tube again just before it was finally sealed. The mother liquors removed from the minus side of the crystallizing system were also run to dryness, dehydrated, and sealed in tubes for measurements. Instead of operating continuously the high-grade crystallizing system of bromides, the system was closed up for each lot of intermediates received from the plant laboratory. All liquors remaining after about 80 per cent of the mesothorium had been removed as a finished product were evaporated to dryness, dehydrated, and finally sealed in weighed tubes.

After the various salts had aged for a month, the activity of each was determined by the gamma-ray method of comparison with radium standards. The data in hand were then arranged in the form of a balance sheet, as shown in Table 10. In the course of the fractionations some of the solutions needed to be filtered. Crystals

sometimes crept over the sides of a dish. A small sponge was used to wipe up any material that appeared on the glass plate on which the crystallizing dishes were arranged. These liquors were all filtered before being returned to the system. The papers with small residues that accumulated thus were ashed and sealed. They appear in the balance sheet under the caption "ashes, etc." Table 11 gives details of values taken out.

TABLE 10.—*Higher fractionations of bromides (eighth series).*[a]

Item.	Grams.	Mg. (Ra equivalent).
Mesothorium and radium put in:		
18 tubes of intermediates	70.347	258.3
Ashes, from seventh series	.232	2.5
Intermediate bromides, seventh series	6.384	25.5
Total input	76.963	286.3
Values taken out:		
High-grade tubes 1, 2, 3, 4	1.6182	210.6
Bromide tails, tubes 1, 2, 3, 4, 5, 6	69.223	4.8
Ashes, etc	.384	4.7
Radiothorium	.072	4.6
Intermediates, two tubes for ninth series	5.8982	64.0
Total values taken out	77.195	288.7

[a] These experimental data were obtained by Mr. G. F. Brechenridge, who fractionated this series of bromides in the chemical laboratory of the University of Missouri.

TABLE 11.—*Details of values taken out in higher fractionations of bromides (eighth series).*

Tube No.—	Contents (grams).	Mg. (radium equivalent).	Mg. per gram.
HIGH-GRADE TUBES.			
1	0.2695	54.1	200.8
2	.3678	68.5	186.4
3	.7655	55.3	72.2
4	.2154	32.7	152.0
	1.6182	210.6	
BROMIDE TAILS.			
1	15.98	0.5	0.031
2	5.005	.3	.06
3	16.694	.4	.024
4	12.425	.3	.024
5	9.046	2.5	.28
6	10.073	.8	.08
	69.223	4.8	
INTERMEDIATES.			
1	3.8246	37.5	
2	2.0736	26.5	
	5.8982	64.0	

In most of the fractionations, the activity of the products taken out exceeded by several milligrams the values introduced: in one series, however, nearly three milligrams were not recovered. That apparently more mesothorium was recovered in the final refining than was used in the beginning may be explained partly by the growth of radiothorium in the products during the period of fractionation. (See pages 49 and 51.) Tubes of intermediate bromides were often five times as long as the radium standard used for comparison and, again, no correction was made for absorption of gamma radiation by the barium bromide itself in measuring the activity of the intermediate bromides. Any one of these factors will account for the increase observed.

RELATION OF ALPHA AND GAMMA RAY ACTIVITY OF MESOTHORIUM AND RADIUM.

The investigation of Meitner (7) on the half-life periods of mesothorium and radiothorium also furnished data for comparisons of the ratios of the alpha and gamma radiations from radiothorium and radium. Meitner's results have special value in connection with the use of mesothorium instead of radium in the production of luminous paints where the apha-ray activity is the deciding factor.

To obtain data for comparison of the alpha and gamma radiations of radiothorium and radium, Meitner devised the following procedure: The gamma-ray activity of a fresh specimen of mesothorium free from radium was found to be equivalent to 6.32×10^{-5} mg. of radium. From measurements on the growth of the alpha-ray activity in specimens of mesothorium, Meitner calculated that the alpha-ray activity of the radiothorium in equilibrium with 6.32×10^{-5} mg. of mesothorium is equivalent to 15.4×10^{-5} mg. of radium. In these experiments, the alpha-ray activity of radium and its short lived products was measured under the same conditions as the alpha-ray activity of radiothorium. To obtain the gamma-ray activity of the radiothorium in equilibrium with 6.32×10^{-5} mg. of mesothorium, Meitner employed the factor 1.513 given by Meyer and Hess (15), who state that the gamma rays from radiothorium (ThD) produce 1.513 times the effect of the gamma rays of mesothorium (MsTh2) when measurements are made through 0.5 cm. of lead. Hence, the gamma-ray activity of the radiothorium in equilibrium with 6.32×10^{-5} mg. of mesothorium is given by the equation $6.32\times10^{-5}\times 1.513=9.56\times10^{-5}$ mg. of radium. As the alpha-ray activity of this amount of radiothorium was found to be equivalent to that of 15.4×10^{-5} mg. of radium, it is seen that for equal gamma-ray activities the alpha-ray activity of radiothorium is fully 1.6 times that of radium. Furthermore, it follows that the alpha-ray activity of the

radiothorium in equilibrium with the mesothorium (expressed in terms of radium) in a mineral is given by the ratio $\frac{15.4\times10^{-5}}{6.32\times10^{-5}}$ or 2.44.

It will be of further interest to apply this treatment in estimating the alpha-ray activity of specimens of mesothorium of different ages. As an example, let us assume that 20 per cent of the gamma activity of a commercial sample of mesothorium a month old is contributed by radium. From Table 17 (p. 52), which gives the growth of radiothorium in specimens of mesothorium, it is found that 0.289 of the equilibrium amount of radiothorium has accumulated after the lapse of a year. At this time the alpha-ray activity contributed by the radiothorium present will correspond to approximately $2.44\times0.8\times.29$ or 0.57 mg. of radium per milligram of original gamma-ray activity, and the total alpha-ray activity will be about 0.77 that of radium. After a period of two years, when 0.46 of the equilibrium amount of radiothorium has accummulated, the alpha-ray activity will be very nearly 1.1 times that of radium; and at the time of maximum alpha-ray activity—after 4.83 years, when 0.61 of the equilibrium amount of radiothorium is present—the alpha-ray activity becomes about 1.4 times that of radium. At 10 years of age the alpha-ray activity will still exceed slightly that of radium.

In the foregoing computations we have neglected the quantity of radiothorium that is present in specimens of mesothorium at the time they are standardized against radium. By reference to Table 17 it is seen that the radiothorium present in freshly prepared samples of mesothorium contributes about 4 per cent of the gamma radiation at the time such preparations are usually standardized, about 40 days after final crystallization and sealing. In other words, of the 80 per cent of gamma-ray activity, 4 per cent is contributed by radiothorium leaving an initial amount of mesothorium equivalent to 0.77 mg. of radium to be employed instead of 0.8 in more rigorous computations.

A somewhat different relation between the alpha and gamma activities of mesothorium preparations and radium is derived by considering the factor 1.81 found by McCoy and Cartledge (38) for the gamma-ray effect of radiothorium when expressed in terms of radium. Applying the factor 1.81 to the data of Meitner it follows that the gamma-ray activity of the radiothorium in equilibrium with 6.32×10^{-5} mg. of mesothorium would be 11.4×10^{-5} mg. radium, and its alpha-ray activity would then be only 1.26 times that of radium. But inasmuch as mesothorium is sold on the basis of gamma-ray measurements made when only 4 per cent of the gamma radiation is contributed by radiothorium, the examples illus-

trating the alpha-ray activity of specimens of mesothorium with age are not affected by the factor for the relative activity of the gamma rays of radiothorium and radium.

Still a different relation, Meitner points out, exists between the alpha and gamma rays of radiothorium and radium when instead of comparing the ionization produced by the alpha rays, the actual number of alpha particles from radiothorium and radium is considered.

Atom for atom, radiothorium and its transformation products emit five alpha particles to four from radium and its short-lived products. The relative ionization produced by the two groups of alpha particles can be readily calculated. The number of ions, N produced in air by an alpha particle is given by the formula

$$N = aR^{2/3}$$

R, being the range of the alpha particle in air at standard temperature and pressure, and a, constant whose value is 7.08×10^4. Applying this formula one finds that the ions produced in air by the four alpha particles from radium amount to 7.49×10^5, and for the five alpha particles from radiothorium the sum is 9.98×10^5. Hence, atom for atom, the ionization produced by the alpha particles from radiothorium is 1.33 greater than that from radium.

Stating this relation in another way, N atoms of radium plus products produce A ions; N atoms of radiothorium plus products produce 1.33 A ions: whence $\frac{N}{1.33}$ atoms of radiothorium plus products produce A ions, N being the number of atoms of radium disintegrating per second. In other words, the amount of radiothorium that emits the same number of alpha particles per second as a given quantity of radium is 1.33 times greater than the amount of radiothorium whose alpha-ray activity equals that of the radium. Consequently the gamma-ray activity of radiothorium is atom for atom, 1.33 times greater than for equal alpha-ray activities.

Applying this ratio to the experimental data of Meitner (7) it is seen that atom for atom, $1.33 \times 6.32 \times 10^{-5} = 8.4 \times 10^{-5}$ mg. of mesothorium, and $1.33 \times 1.513 \times 6.32 \times 10^{-5} = 12.7 \times 10^{-5}$ mg. of radiothorium will each be equivalent to 15.4×10^{-5} mg. of radium. Atom for atom, the gamma activity of radium is (1) only 1.21 times that of radiothorium, (2) 1.83 times that of mesothorium, and (3) 0.72 times that of mesothorium and radiothorium in equilibrium.

A commercial sample of mesothorium standardized about a month after its preparation and containing 20 per cent radium when a year old contains 0.289 of the equilibrium amount (see Table 17, p. 52) of radiothorium. The number of radium and radiothorium atoms changing per second in comparison with radium as

unity will be given by the formula: $0.2+0.289\times0.77\times1.83=0.61$. In mesothorium two years old, the number is 0.85; at the time of maximum radiothorium, 1.05; and after a period of ten years, 0.85.

The actual number of alpha particles emitted per second in comparison with radium, from a mesothorium one year old, assuming that 20 per cent of its gamma-ray activity at the time it was standardized was contributed by the radium present, will be given by the equation

$$0.2+0.289\times0.77\times1.83\times5/4=.71.$$

In other words, the number of scintillations per second 1 mg. of mesothorium—20 per cent radium—produces a year after it was standardized is about 70 per cent that of 1 mg. of radium.

RATING OF MESOTHORIUM IN TERMS OF RADIUM BY GAMMA-RAY MEASUREMENTS.

Inasmuch as two members of the thorium series, mesothorium 2 and thorium D, emit penetrating gamma rays to one member, radium C of the radium series, the gamma activity of specimens of mesothorium depends first of all upon the proportion of the gamma rays contributed by mesothorium 2 and thorium D, which is governed by the age of the specimen. In addition the gamma-ray activity of a specimen of mesothorium in terms of radium depends to some extent upon the experimental conditions under which the measurements are made. Moreover the gamma rays from RaB, the penetrating power of which averages about one-tenth that of the rays from RaC, should be considered when comparison measurements are made with lead screens less than 1 centimeter in thickness. Other factors remaining constant variations in the thickness of the screen, interposed when comparisons are being made, will make a difference in the rating of the specimen of mesothorium, indicating that the absorption coefficients (see Table 1, p. 7) for gamma rays do not remain constant, and that the coefficients for radium C, mesothorium 2, and thorium D vary differently. The complex nature of the problem becomes more evident in examining the investgations of Meyer and Hess (15) in this field, as summarized on page 44.

Hahn (52), who studied the problem with the object of distinguishing between radium and specimens of mesothorium of different ages, determined the absorption curves of five specimens, using as screens lead cylinders of different wall thickness. The specimens included (1) pure radium bromide; (2) commercial mesothorium bromide about a month old; (3) commercial mesothorium two years old; (4) mesothorium bromide freshly prepared, that is, about a month old, free from radium; (5) radiothorium free from mesothorium. The absorption curves for the five specimens were constructed on such a

scale that the radiation in the electroscope without screening was given the value 100, the rays having traversed the 3.3 mm. lead wall of the electroscope.

The characteristic absorption curves showed that the different specimens of mesothorium could be distinguished effectively and with certainty from radium, and from one another. In order to work with certainty, however, as Hahn points out, it is necessary to compare specimens of nearly the same activity.

To illustrate how dependent the rating value of mesothorium is upon the thickness of the lead screen, interposed in making comparison with the gamma rays of radium, the values of the radiation observed through 45 mm. of lead were reduced to the scale, radium equals 100. The relations are shown in Table 12.

TABLE 12.—*Relation of gamma-ray activity of mesothorium and radium.*

Specimen.	No screen besides 3.3 mm. lead wall.	Gamma-ray through 45 mm. Pb.
Radium	100	100
Fresh MsTh (commercial)	100	83.4
MsTh (2 years old)	100	101.1
Fresh MsTh (free from Ra)	100	75.5
Radiothorium	100	138

EXPERIMENTS OF MEYER AND HESS.

In rating mesothorium Meyer and Hess screened the specimen on one side by large lead plates, the specimen resting on the lead screen. The radiation passing through the plates was calculated by an established formula involving constant values for the absorption coefficients of the gamma rays from RaC, MsTh 2, and ThD.

The gamma-ray activity of specimens of different ages in terms of radium was finally derived by introducing certain factors in the equation expressing the ionization current, namely, $I=\lambda_1 MsTh+K\lambda_2 RaTh$. The factors employed represent the relative penetrating power of the gamma rays of mesothorium 2, to radium C, and mesothorium 2 to thorium D. The derivation of these factors and their use are illustrated in Table 15 (p. 48), which shows the gamma activity of mesothorium of different ages based upon comparison with radium when measured through different thicknesses of lead.

APPARATUS.

The experimental arrangement of apparatus devised by Meyer and Hess is shown in figure 3. The ionization chamber consists of a shallow circular vessel made of zinc, 30 cm. in diameter, fitted to a Wulf

quartz-fiber electrometer. The electrode was a circular disk of sheet zinc 28 cm. in diameter.

KING'S ABSORPTION FORMULA (53).

When the specimen rests directly on the absorbing screen, the absorption does not take place according to a simple exponential

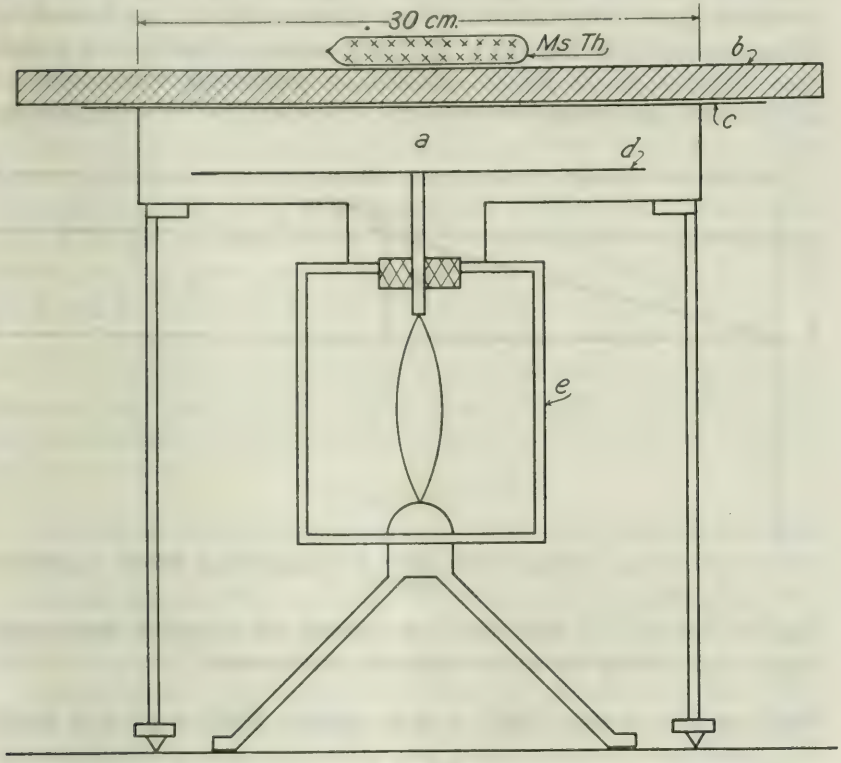


FIGURE 3.—Apparatus designed by Meyer and Hess for rating mesothorium: *a*, Ionization chamber; *b*, lead; *c*, zinc sheet; *d*, zinc disk; *e*, Wulf electrometer.

formula. For the experimental arrangement of Meyer and Hess, the following simplified formula of King applies:

$$I_t = \frac{f(uT)}{1-\cos\theta}$$

where I_t is the current produced after passage through a thickness t of the screen, and θ is the angle shown in figure 4.

$$f(x) = e^{-x} + x\int_{\infty}^{x} \frac{e^{-x}}{x} dx$$

APPLICATION OF KING'S FORMULA.

To test the applicability of King's formula, Meyer and Hess measured the absorption of the gamma rays from the following sources, in the apparatus figured, using screens of zinc and lead: (1) Radium (RaC); (2) pure radiothorium (ThD); (3) mesothorium free from radium and radiothorium (MsTh 2). The measurements gave values showing that agreement with the formula of King was not obtained when the usual values of Soddy and Russell (see Table 1, p. 7) for the absorption coefficients were used. A satisfactory agreement however appeared when the following absorp-

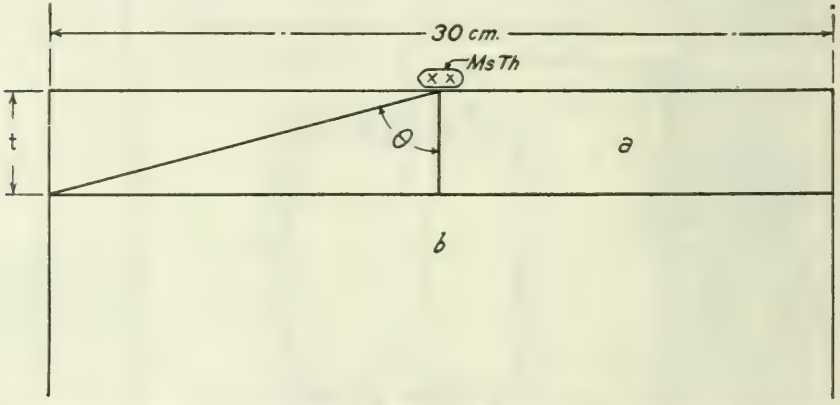


FIGURE 4.—Ionization chamber of the Meyer-Hess apparatus: *a*, Screen; *b*, ionization chamber.

tion coefficients for lead were introduced, all of which were materially higher than the older values in parenthesis:

ThD, μ—0.58 (0.462): RaC, μ—0.64 (0.50): MsTh 2, μ—0.75 (0.62)

The higher values were used by Meyer and Hess in their calculations. The calculated values for the ionization current were reduced to the scale where I=1.000, when no screen intervenes, for each substance. The ratio of the values for ThD and MsTh 2—that is $\frac{\text{ThD}}{\text{MsTh 2}}$ gave the values of the factor K to be used in the equation for the current $I_t=\lambda_1 M+K\lambda_2 R$, for different thicknesses of lead. In other words the factor K expressed the gamma radiation from ThD in terms of MsTh 2. To express the combined gamma radiation from MsTh 2 and ThD in terms of radium, the ratio $\frac{\text{MsTh 2}}{\text{RaC}}$ was introduced. This ratio is designated by K′. That is, the products $K'I_t$ gave the value of the ionization current of specimens of mesothorium at various ages in terms of radium when measurements

were made with lead screens of different thicknesses. The values of K and K′ corresponding to different thicknesses of lead are given in Table 13.

TABLE 13.—*Values for the constants K and K′.*

t (cm) =	0.0	0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0
K =	1.00	1.17	1.325	1.47	1.62	1.795	1.96	2.34	2.70
K′ =	1.00	.91	.843	.79	.74	.69	.65	.58	.525

Apply the constants K and K′ to a concrete case, for example, a specimen of mesothorium free from radium, age two years, measured through 1.0 cm. of lead. If the initial current, when no radiothorium has accumulated, is arbitrarily considered equal to 1.00, then after the lapse of two years the current I is represented by $I=f_1+Kf^2$ (see Table 17, p. 52) f_1 is the fraction of mesothorium remaining, and f_2 is the fraction of the equilibrium amount of radiothorium corresponding to the initial mesothorium. Introducing the values of f_1 and f_2 from Table 17, and K from Table 13, we have

$$I=0.814+1.32\times0.462=1.42.$$

which means that the gamma-ray activity of the specimen after the lapse of two years is 1.42 greater than initially. But when mesothorium is rated in terms of radium, then the activity of the two-year old specimen is

$$K'I=0.84\times1.43=1.19.$$

The initial rating of the sample, in terms of radium being equal to unity, would have been 0.84, when screened by 1.0 cm. of lead.

The assumption, that for t=0, the effect of the individual types of gamma rays is the same, that is, K=1, is not well founded, however, but it serves to illustrate the variations that may occur.

In seeking an explanation for the ionization produced by gamma rays, it is but natural to assume that the less penetrating primary rays, which are absorbed by the gas in the chamber in proportion to their higher absorption coefficients, would produce a correspondingly greater ionization. This assumption is not borne out, however, by experiment. Meyer and Hess (15) point out that the intensity of the entering gamma rays seems to be the governing factor, and therefore they regard the ionization in the chamber as the result of soft secondary rays; in other words, the release of such rays is proportional to the penetrating power of the gamma rays, that is, to $1/\mu$. The values of K and K′ will then be replaced by the following factors:

$$K_1=\frac{0.75}{0.58}K=1.293\ K$$

$$K'_1=\frac{0.64}{0.75}K'=0.853\ K'$$

The values of K_1 and K'_1, for different thicknesses of screen appear in Table 14.

TABLE 14.—*Values of the constants K_1 and K'_1.*

t (cms.)=	0.00	0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0
K_1=	1.293	1.513	1.713	1.901	2.095	2.321	2.534	3.019	3.491
K'_1=	.853	.776	.719	.674	.631	.589	.555	.494	.448

Employing the method of calculating the gamma-ray activity of mesothorium in terms of radium, used in the example above to illustrate the way Meyer and Hess introduced the factors K and K′, a table similar to one of theirs has been prepared using the factors K_1 and K'_1 as they have done, but using the radioactive constants of Meitner (7) for mesothorium and radiothorium instead of the older values (see Table 17, p. 52, and the example following Table 13).

TABLE 15.—*Rating of mesothorium, free from radium in terms of radium, at various ages, by absorption measurements with lead screens of different thicknesses.*

Age (years).	0.0	0.5	1.0	2.0	3.0	4.0
Gamma activity I.	$I=f_1+K_1f_2=1.000.$	$0.950-0.162\ K_1$	$0.902-0.289\ K_1$	$0.814+0.461\ K_1$	$0.734-0.554\ K_1$	$0.662+0.591\ K_1$
	GAMMA-RAY ACTIVITY IN TERMS OF RADIUM (VALUES OF K'_1).					
t (cm. of lead).						
0.0	0.853	0.989	1.088	1.203	1.237	1.216
.5	.776	.927	1.039	1.172	1.220	1.208
1.0	.719	.883	1.005	1.153	1.210	1.204
1.5	.674	.848	.978	1.140	1.204	1.203
2.0	.631	.814	.951	1.123	1.192	1.199
2.5	.588	.780	.925	1.108	1.188	1.199
3.0	.555	.755	.907	1.100	1.187	1.200
4.0	.494	.711	.876	1.092	1.190	1.209
5.0	.448	.679	.856	1.086	1.195	1.222

Age (years).	5.0	6.0	8.0	10	15
Gamma activity I.	$0.597+0.606\ K_1$.	$0.538+0.592\ K_1$.	$0.438+0.534\ K_1$.	$0.356+0.459\ K_1$.	$0.213+0.291\ K_1$.
	GAMMA-RAY ACTIVITY IN TERMS OF RADIUM (VALUES OF K'_1).				
t (cm. of lead).					
0.0	1.178	1.112	0.962	0.810	0.502
.5	1.175	1.113	.964	.815	.506
1.0	1.176	1.116	.970	.821	.511
1.5	1.179	1.121	.979	.828	.519
2.0	1.179	1.122	.983	.831	.520
2.5	1.179	1.124	.987	.836	.522
3.0	1.183	1.131	.994	.843	.528
4.0	1.199	1.149	1.013	.861	.539
5.0	1.215	1.166	1.031	.878	.551

Table 15 shows that specimens of mesothorium less than a year old are underrated on the radium standard, even when screens of lead only 0.5 cm. in thickness are used in making the gamma-ray comparisons; when rather thick screens of lead are used, the ratings of such specimens are considerably too low. Then, till the age of about seven years is reached, these specimens are rated too high,

whereas later they are again rated too low. Meyer and Hess further note that the results show clearly how the marked influence of the screen thickness gradually diminishes as the specimens age, and finally change sign. In the period from two to six years, specimens of mesothorium will be rated from 10 to 20 per cent too high on the radium standard.

In support of the relations shown in the table, Meyer and Hess assert that measurements made with a specimen of mesothorium about one-half year old, and another, nearly two years after its last crystallization as bromide, confirmed satisfactorily the data given in the preceding table. The differences would be reduced, of course, if the mesothorium compounds contained radium; if, for example, the gamma-ray activity of the radium approximated 20 per cent, then the differences in the table would be reduced to four-fifths of the values given.

According to the table, fresh specimens of mesothorium when standardized against radium by gamma-ray measurements made through a thickness of 0.5 cm. of lead are rated at 0.777 of the value corrected for differences in absorption. Consequently, when the initial rating of mesothorium according to the prevailing practice is arbitrarily taken as unity, the change in gamma-ray activity with age, if comparisons are made against radium through 0.5 cm. of lead, will show correspondingly greatly variations, as is shown in Table 16, column 2, where the values in the preceding table corresponding to 0.5 cm. of lead have been adjusted to the initial value 1.000. The same values are, of course, obtained by employing directly the following formula: $I=f_1+Kf_2$, where K has the value 1.513. For the sake of comparison there has been included in the table, third column, the gamma-ray activity computed with the factor 1.81 given by McCoy and Cartledge (38), whose gamma-ray measurements were made through 2.03 mm. of lead and 1.32 mm. of brass. The factor of Meyer and Hess for this equivalent of screen would be lower than 1.513, probably about 1.4.

TABLE 16.—*Variations in the gamma-ray activity of mesothorium free from radium, at various ages, by absorption in 0.5 cm. of lead.*

Age (years).	K=1.513 (Meyer and Hess).	K=1.81 (McCoy and Cartledge).
0.0	1.000	1.000
.5	1.195	1.244
1	1.339	1.425
2	1.513	1.650
3	1.514	1.739
4	1.567	1.744
5	1.515	1.696
6	1.435	1.611
8	1.249	1.408
10	1.054	1.119
15	.665	.741

The differences in the values of K may be partly due to experimental conditions. Perhaps other assumptions with reference to the factors K_1 and K'_1 of Meyer and Hess may have to be introduced. For example, in direct comparison of the gamma radiation of mesothorium with radium standards, the effect of the gamma rays from RaB should not be neglected for screens of lead less than 1 cm. in thickness. Again, in rating mesothorium, the lead screens are generally placed close to the electroscope and the specimen and radium standard at suitable distances from the screen. As this experimental arrangement differs from that of Meyer and Hess, their tables may have but limited application. At all events, it seems desirable to conduct further experiments on the variation of the gamma-ray activity of mesothorium with age, as well as the relation of its gamma-ray activity to its alpha radiation.

MAXIMA OF ALPHA AND GAMMA RAY ACTIVITY.

ALPHA-RAY ACTIVITY.

As the alpha-ray activity of mesothorium is governed by the growth of radiothorium R in the specimen, which is given at any time by the relation (32),

$$R_t=\frac{M\lambda_1}{\lambda_2-\lambda_1}(e^{-\lambda_1 t}-e^{-\lambda_2 t})$$

its maximum value $\frac{d R_t}{d t}=0$, is reached at the time t, when

$$\lambda_1 e^{-\lambda_1 t}=\lambda_2 e^{-\lambda_2 t}$$

where $\lambda_1=0.1032$ and λ_2 0.364. Solving for t, we find the value 4.83 years. A specimen of mesothorium originally free from radiothorium attains its maximum alpha-ray activity after 4.83 years. The presence of radium in the specimen, though important in the total alpha radiation, as shown in the examples previously given, practically has no effect on the time the maximum alpha-ray activity is reached.

GAMMA-RAY ACTIVITY.

The gamma-ray activity of a specimen of mesothorium originally free from radiothorium and of initial activity, I_0, is given by the equation,

$$I_t=I_0 e^{-\lambda_1 t}+K\frac{\lambda_2}{\lambda_2-\lambda_1}(e^{-\lambda_1 t}-e^{-\lambda_2 t})$$

in which the factor K represents the relative gamma-ray effect of thorium D to mesothorium 2. The time of maximum t when $\frac{d I_t}{d t}=0$, is given by the relation

$$e^{(\lambda_1-\lambda_2)t}=\frac{\lambda_1}{\lambda_2}\left(\frac{K+1}{K}-\frac{\lambda_1}{\lambda_2 K}\right)$$

It is seen that the time of maximum gamma-ray activity depends upon the value assigned to K. When K=1.513, T=3.34 years; for K=1.81, t=3.55 years; when K=$\frac{\lambda_1}{\lambda_2}$, t=0; for K=1, t=2.76 years.

The foregoing summaries of the investigations of Meyer and Hess, McCoy and Henderson, McCoy and Cartledge, and Meitner taken collectively go to show that complicated relations exist for the gamma-ray activity of mesothorium and its relation to the alpha radiation. It is hoped that further experimental studies will be undertaken to verify the splendid contribution of these pioneer workers and to extend the knowledge of how the different types of radiations of the thorium series are related to one another and to the members of the uranium-radium series.

GROWTH OF RADIOTHORIUM IN MESOTHORIUM PREPARATIONS.

If the gamma activity of a sample of mesothorium is called unity at the time it has reached equilibrium with mesothorium 2, three days after separation, then its activity A, after an interval, t, is given

$$A=f_1+K\ f_2 \quad (38) \qquad (1)$$

where, at the time, t, f_1 is the fraction of the initial amount of mesothorium, and f_2 is the fraction of the amount of radiothorium that would be in equilibrium with the initial amount of mesothorium in a mineral.

Equation 1 involves the following considerations: Let M_o represent the initial amount of mesothorium; M, the amount after an interval of t years; then $M/M_o=f_1$, and since $M=M_{oe}-\lambda_1 t$ where λ_1 is the radioactive constant of mesothorium 1, $f_1=e-\lambda_1 t$. Let R_o stand for the amount of radiothorium (that is, atoms of radiothorium) that would be in equilibrium with the initial amount of mesothorium, M_o in a mineral; and R, the amount of radiothorium present at the time, t, when the initial amount of mesothorium has decayed to the value of M. In other words, R is the amount of radiothorium that has accumulated in the specimen of mesothorium during the period of t years. $R/R_o=f_2$. Let λ_1, 0.103, and λ_2, 0.364, denote, respectively, the radioactive constant of mesothorium 1 and radiothorium.

The total gamma-ray activity at the time, t, is given by

$$A=\lambda_1 M+ K \lambda_2 R.$$

where K, a constant, determined experimentally, denotes the proportional gamma-ray effect contributed by the Th D when equilibrium exists with thorium in a mineral. The value of K will also depend

on the thickness of screen employed in making the measurements, and probably on other factors.

The second term, f_2, in equation 1 is found from the values of R and R_o. The amount of radiothorium, R, that has accumulated during the interval T, is given by the equation

$$R=\frac{M_0\lambda_1}{\lambda_2-\lambda_1}(e^{-\lambda_1 t}-e^{-\lambda_2 t}) \quad . \quad . \quad . \quad . \quad (2)$$

For equilibrium between mesothorium and radiothorium we have the relation

$$\lambda_1 M_0=\lambda_2 R_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

When λM_o is put equal to 1, and equation 3 is then combined with equation 2, we obtain

$$f_2=\frac{\lambda_2}{\lambda_2-\lambda_1}(e^{-\lambda_1 t}-e^{-\lambda_2 t}) \quad . \quad . \quad . \quad . \quad (4)$$

and as the activity of the radiothorium present, R, may also be expressed as $K\lambda_2 R$, it is apparent from the relations in 2, 3, and 4 that the gamma activity of the radiothorium R, is Kf_2 and the total gamma activity A is

$$A=f_1+Kf_2$$

In Table 17, which follows, are given the values of f_1 and f_e, with Meitner's (7) values for the radioactive constants of mesothorium and the radiothorium. The values for $e^{-\lambda_2 t}$ show the decay of pure radiothorium. In the third column we have the corresponding values for mesothorium. The fourth column gives the values of R, calculated from equation 2, and in the last column is the fraction of the amount of radiothorium that would be in equilibrium with unit quantity of mesothorium in a mineral.

$\frac{\lambda_1}{\lambda_2-\lambda_1}=0.3956$ (log. 9.59727—10); $\frac{\lambda_2}{\lambda_2-\lambda_1}=1.396$ (log. 0.14479); R_o from equation 3=0.284.

TABLE 17.—*Decay of radiothorium and mesothorium and growth of radiothorium in mesothorium preparations.*

T.	$e^{-\lambda_2 t}$	$e^{-\lambda_1 t}=f_1$	R.	$R/R_0=f_2$
MONTHS.				
0	1.000	1.000	0.0	0.0
1	.970	.9915	.0085	.0299
2	.941	.983	.0166	.0585
3	.913	.975	.0243	.0855
4	.886	.966	.0316	.111
5	.859	.958	.0392	.138
6	.834	.950	.0459	.162
9	.761	.926	.0651	.230
YEARS.				
1	.695	.902	.0819	.289
1.5	.579	.857	.110	.387
1.905	.500	.822	.127	.448
2	.483	.814	.131	.461
2.5	.403	.773	.146	.515
3	.336	.734	.157	.554
3.5	.280	.697	.165	.580
4	.233	.662	.170	.591
4.5	.194	.628	.173	.604
5	.162	.597	.172	.606
5.5	.135	.567	.171	.601
6	.113	.538	.168	.592

TABLE 17.—*Decay of radiothorium and mesothorium and growth of radiothorium in mesothorium preparations*—Continued.

T.	$e^{-\lambda_2 t}$	$e^{-\lambda_1 t}=f_1$	R.	$R/R_0=f_2$
6.7	.087	.500	.163	.575
7	.078	.486	.161	.568
8	.054	.438	.152	.534
9	.038	.395	.141	.497
10	.026	.356	.131	.459
12	.013	.290	.110	.386
15	.004	.213	.083	.291
20	.....	.127	.050	.175
25	.....	.076	.030	.106
30	.....	.045	.0178	.063
40	.....	.016	.0063	.022
50	.....	.006	.0023	.008

TABLE 18.—*Decay and growth of mesothorium 2* ($\lambda=.112\ hr.^{-1}$).

Time, T, hours.	Decay.	Growth.	Time, T, hours.	Decay.	Growth.
0.0	100.0	0.0	12	26.1	73.9
0.25	97.2	2.8	13	23.4	76.6
0.50	94.6	5.4	14	20.9	79.1
0.75	92.0	8.0	15	18.7	81.3
1.0	89.4	10.6	16	16.7	83.3
1.5	84.6	15.4	17	14.9	85.1
2.0	79.9	20.1	18	13.3	86.7
2.5	75.6	24.4	19	11.9	88.1
3.0	71.5	28.5	20	10.7	89.3
3.5	67.6	32.4	21	9.5	90.5
4.0	63.9	36.1	22	8.5	91.5
4.5	60.4	39.6	23	7.6	92.4
5.0	57.1	42.9	24	6.8	93.2
5.5	54.0	46.0	26	5.5	94.5
6.0	51.1	48.9	28	4.4	95.6
6.2	50.0	50.0	30	3.5	96.5
7	45.7	54.3	33	2.5	97.5
8	40.8	59.2	36	1.8	98.2
9	36.5	63.5	40	1.1	98.9
10	32.7	67.3	48	.46	99.5
11	29.2	70.8			

TABLE 19.—*Decay and growth of thorium X* ($\lambda=0.00792\ hr.^{-1}=0.190\ d.^{-1}$).

Time (hours).	Decay.	Growth.	Time (days).	Decay.	Growth.
0	100	0	1¾	72.9	27.1
1	99.2	0.8	2	68.4	31.6
2	98.4	1.6	2¼	62.2	37.8
3	97.7	2.3	3	56.6	43.4
4	96.9	3.1	3¼	51.4	48.6
5	96.1	3.9	3.65	50.0	50.0
6	95.4	4.6	4	46.8	53.2
7	94.6	5.4	4¼	42.5	57.5
8	93.9	6.1	5	38.7	61.3
9	93.1	6.9	6	32.0	68.0
10	92.4	7.6	7	26.5	73.5
12	90.9	9.1	8	21.9	78.1
14	89.5	10.5	9	18.1	81.9
16	88.1	12.9	10	15.0	85.0
18	86.7	13.3	12	10.2	89.8
20	85.4	14.6	15	5.8	94.2
22	84.0	16.0	18	3.3	96.7
24	82.7	17.3	21	1.85	98.15
27	80.8	19.2	24	1.05	98.95
30	78.9	21.1	30	.36	99.64
33	77.0	23.0	40	.05	99.95
36	75.2	24.8			

BIBLIOGRAPHY.

1. Soddy, Frederick, The radio elements and the periodic law: Chem. News, vol. 107, 1913, pp. 97–99; and Die Radioelemente und das periodische Gesetz: Radio. Elek., Bd. 10, 1913, pp. 188–197.

Fleck, Alexander, The chemical nature of some radioactive disintegration products: Jour. Chem Soc., vol. 103, 1913, pp. 381–399, 1052–1061.

Russell, A. S., Periodic system and the radio elements: Chem. News, vol. 107, 1913, pp. 49–52.

Fajans, K. von, Über eine Beziehung zwischen der Art einer radioaktiven Umwandlung und dem elektrochemishen Verhalten der betreffenden der Radioelemente: Physik. Ztschr, Jahrg. 14, 1913, pp. 131–136; Die Stellung der Radioelemente im periodischen System, pp. 136–142.

Hevesey, von G. v., Die Valenz der Radiolemente: Physik. Ztschr. Jahrg. 14, 1913, pp. 49–62.

2. Soddy, Frederick, The radio-elements and the periodic law: Chem. News, vol. 107, 1913, pp. 97–99; also published in Radio. Elek., Bd. 10, 1913, pp. 188–197.

3. Taylor, T. S., On the ionization of different gases by the alpha particles from polonium and the relative amounts of energy required to produce an ion: Phil. Mag., vol. 21, 1911, pp. 571–579; On the retardation of alpha rays by metals and gases: Am. Jour. Sci., vol. 28, 1909, pp. 357–372.

4. Geiger, Hans and Rutherford, Ernest, The number of alpha particles emitted by uranium and thorium and by uranium minerals: Phil. Mag., vol. 20, 1910, pp. 691–698.

5. McCoy, H. N., The periods of transformation of uranium and thorium: Physical Rev., ser. 2, vol. 1, 1913, pp. 401–404.

6. Heiman, Bertha, Über die Lebensdauer des thoriums: Sitzb. Akad. Wiss. Wien. Bd. 123, Abt. IIa, 1914, pp. 1369–1372.

7. Meitner, L., Die Lebensdauer von Radiothor, Mesothor, und Thorium: Physik. Ztsch., Jahrg. 19, 1918, pp. 257–263.

8. Geiger, H., and Nuttall, J. M., The ranges of the alpha particles from various radioactive substances and a relation between range and period of transformation: Phil. Mag. vol. 22, 1911, pp. 613–621.

9. McCoy, H. N., and Ross, W. H., Specific radio activity of thorium and the variation of the activity with chemical treatment and with time: Jour. Am. Chem. Soc., vol. 29, 1907, pp. 1709–1718; Specific radioactivity of uranium; pp. 1698–1709.

10. Hahn, Otto von, Über das Mesothorium: Physik. Ztschr., Jahrg. 9, 1908, pp. 392–404.

11. Hahn, Otto von, Ein Kurzlebiges Zwischenprodukt zwischen Mesothor- und Radiothor: Physik. Ztschr., Jahrg. 9, 1908, pp. 246–248.

12. Hahn, Otto von, und Meitner, Lise, Über die Absorption der Beta Strahlen einiger Radioelemente: Physik. Ztschr., Jahrg. 9, 1908, pp. 321–333.

13. Russell, A. S., and Soddy, Frederick, The gamma rays of thorium and actinium: Phil. Mag., vol. 21, 1911, pp. 130–154.

14. Rutherford, Ernest, and Richardson, H., Analysis of the gamma ray of the thorium and actinium product: Phil. Mag., vol. 26, 1913, pp. 937–948.

15. Meyer, S., and Hess, V. F., Υ-Strahlenmessung von Mesothorpräparaten: Sitzb. Akad. Wiss. Wien. Bd. 123a, Abt. IIa, 1914, p. 1443.

16. Blanc, G. A. von, Die Zerfallskonstante des Radiothoriums: Physik. Ztschr., Jahrg. 8, 1907, pp. 321–324.

17. Meyer, —, and Paneth, —, Notiz über die Zerfallenskonstante des Radiothor: Sitzb. Akad. Wiss. Wien., Bd. 125, 1916, p. 1253.

18. Walter, B., Über die Zerfallskonstante des Radiothors: Physik. Ztschr., Jahrg. 18, 1917, pp. 584–585.

19. Rutherford, Ernest, and Soddy, Frederick, The cause and nature of radioactivity: Phil. Mag., vol. 4, 1902, pp. 370–396, and pp. 569–585; The radioactivity of thorium compounds: Jour. Chem. Soc., vol. 81, 1902, pp. 321–350.

20. Lerch, F. von, Über das ThX und die induzierte Thor aktivität: Sitzb. Akad. Wiss. Wien, Jahrg. 114, 1905, pp. 553–585.

21. Levin, M., On the origin of the beta rays emitted by thorium and actinium: Phil. Mag., vol. 12, 1906, pp. 177–188.

22. McCoy, H. N., and Viol, C. H., The chemical properties and relative activities of the radio products of thorium: Phil. Mag., vol. 25, 1913, pp. 333–359.

23. Rutherford, Ernest, A radioactive substance emitted from thorium compounds: Phil. Mag., vol. 49, 1900, pp. 1–14.

24. Le Rossignol, C., and Gimingham, C. T., The rate of decay of thorium emanation: Phil. Mag., vol. 8, 1904, pp. 107–110.

25. Hahn, Otto von, Über ein neues die Emanation des Thoriums gebendes radioaktives Element: Radio. Elek., Bd. 2, 1905, pp. 233–266.

26. Bronson, H. L., Radioactive measurements by a constant deflection method: Am. Jour. Sci., vol. 19, 1905, pp. 185–190.

27. Barratt, T., On the numbers and ranges of the alpha particles emitted by the emanation and active deposit of thorium: Proc. Phys. Soc., vol. 24, 1912, pp. 112–119.

28. Moseley, H. G. J., and Fajans, K., Radioactive products of short life: Phil. Mag., vol. 22, 1911, pp. 629–638.

29 Hahn, Otto von, and Meinter, Lise, Über die Absorption der Beta Strahlen einiger Radioelemente: Physik. Ztschr. Jahrg. 9, 1908, pp. 321–333.

30. Marsden, E., and Darwin, C. G., The transformations of the active deposit of thorium: Proc. Roy. Soc., vol. 87 A, 1912, pp. 17–29.

31. Hahn, Otto von, and Meitner, Lise, Uber die Verteilung der Beta Strahlen auf die einzelnen Produkte des aktiven Niederschlags des Thoriums: Physik. Ztschr., Jahrg. 13, 1912, pp. 390–393.

32. Rutherford, Ernest, Radioactive substances and their radiations. 1913, 699 pp. Radioactive transformations. 1906, 287 pp.

33. McCoy, H. N., and Ross, W. H., The relation between the radioactivity and the composition of thorium compounds: Am. Jour. Sci., vol. 21, 1906, pp. 433–443.

33a Dadourian, H. M., The radioactivity of thorium: Am. Jour. Sci., vol. 21, 1906, pp. 427–432.

33b. Boltwood, B. B., The radioactivity of the salts of radium: Am. Jour. Sci., vol. 21, 1906, pp. 409–426.

34. Kithil, K. L., Monazite, thorium, and mesothorium: Tech. Paper 110, Bureau of Mines, 1915. 32 pp.

35. McCoy, H. N., and Henderson L. M., The ratio of mesothorium to thorium: Jour. Am. Chem. Soc., vol. 40, 1918, pp. 1316–1326.

36. Soddy, Frederick, The chemistry of mesothorium: Jour. Chem. Soc., vol. 99, 1911, pp. 72–83.

37. Rutherford, Ernest, Radium constants on the international standard: Phil. Mag., vol. 28, 1914, p. 322.

38. McCoy, H. N., and Cartledge, G. H., The gamma-ray activity of thorium D: Jour. Am. Chem. Soc., vol. 41, 1919, p. 50.

39. Wulf, Theodore von, Ein neues Elektrometer für statische Ladungen: Part I, Physik. Ztschr., Jahrg. 8, 1907, pp. 246–248; Part III, Jahrg. 10, 1909, pp. 251–254.

40. Leaming, T. H., Schlundt, Herman, and Underwood, Julius, Comparison of the ionization currents, due to equal quantities of radium emination in different types of electroscopes: Trans. Am. Electrochem. Soc., vol. 30, 1916, pp. 365–378.

41. Underwood, J. E., and Schlundt, Herman, An apparatus for the separation of radium emanation and its determination electroscopically: Trans. Am. Electrochem. Soc., vol. 34, 1918, pp. 203–209. Gives details of the apparatus employed for monazite sand and radium concentrates.

42. Cartledge, G. H., A study of the emanation method of determining thorium: Jour. Am. Chem. Soc., vol. 41, 1919, p. 42.

43. Lind, S. C., Practical methods for the determination of radium, Pt. 1, Interchangeable electroscope and its use: Jour. Ind. Eng. Chem., vol. 7, 1915, pp. 406–410; Pt. 2, The emanation method, pp. 1024–1029.

44. Hahn, Otto von. Ein neues Zwischenprodukt in Thorium: Ber. Deut. chem. Gesell., Jahrg. 40, 1907, pp. 1462–1469.

45. Soddy, Frederick, The chemistry of mesothorium: Jour. Chem. Soc., vol. 99, 1911, pp. 72–83.

46. Marckwald, W., Zur Kenntnis der Mesothoriums: Ber, Deut. chem. Gesell., Jahrg. 43, 1910, pp. 3420–3422.

47. Parsons, C. L., Moore, R. B., Lind, S. C., Schaefer, O. C., Extraction and recovery of radium, uranium, and vanadium from carnotite: Bull. 104, Bureau of Mines, 1915. 124 pp.

48. Nierman, J. L., The concentration of radium and mesothorium by fractional crystallization: Jour. Phys. Chem., vol. 24, No. 3, March, 1920, p. 192.

49. McCoy, H. N., U. S. Patent 1,103,600, 1914.

50. McCoy, H. N., and Henderson, L. M., The ratio of mesothorium to thorium: Jour. Am. Chem. Soc., vol. 40, 1918, pp. 1316–1326.

51. Geiger, H., The ionization produced by an alpha particle: Proc. Roy. Soc., vol. 82A, part I, 1909, p. 486 ff. Connection between ionization and absorption: Proc. Roy. Soc., vol. 83A, Part II, pp. 505–515.

52. Hahn, Otto von, Sur la distinction des préparations de radium et des préparations de mesothorium d'inégale ancienneté au moyen de leur rayonnement: Le Radium, t. 11, 1914, pp. 71–74.

53. King, L. V., Note on the cosine law of radiation: Phil. Mag., vol. 23, 1912, p. 245.

54. Soddy, F., The chemistry of the radio-elements, part II, 1914, p. 23.

55. Rutherford, E., and Wood, A. B., Long range alpha particles from thorium: Phil. mag., 6th ser., vol. 31, 1916, p. 379.

56. Scholl, C. E., Crystallization of radium-barium solution: Jour. Am. Chem. Soc., vol. 42, 1920, pp. 889–896.

PUBLICATIONS ON NONFERROUS METALLURGY.

A limited supply of the following publications of the Bureau of Mines has been printed and is available for free distribution until the edition is exhausted. Requests for all publications can not be granted, and to insure equitable distribution applicants are requested to limit their selection to publications that may be of especial interest to them. Requests for publications should be addressed to the Director, Bureau of Mines.

The Bureau of Mines issues a list showing all its publications available for free distribution as well as those obtainable only from the

Superintendent of Documents, Government Printing Office, on payment of the price of printing. Interested persons should apply to the Director, Bureau of Mines, for a copy of the latest list.

PUBLICATIONS AVAILABLE FOR FREE DISTRIBUTION.

BULLETIN 104. Extraction and recovery of radium, uranium, and vanadium from carnotite, by C. L. Parsons, R. B. Moore, S. C. Lind, and O. C. Schaefer. 1915. 124 pp.

BULLETIN 175. Experiment stations of the Bureau of Mines, by Van. H. Manning. 1919. 106 pp., 29 pls., 2 figs.

BULLETIN 187. Treatment of tungsten ores of Boulder County, Colo., by J. B. Bonardi and J. C. Williams. 1921. 77 pp., 18 pls., 10 figs.

BULLETIN 202. Electric brass-furnace practice, by H. E. Gillett and E. L. Mack. 1922. 320 pp., 25 pls., 35 figs.

TECHNICAL PAPER 182. Flotation of chalcopyrite in chalcopyrite-pyrrhotite ores of southern Oregon, by Will H. Coghill. 1918. 13 pp., 1 fig.

TECHNICAL PAPER 230. The determination of molybdenum, by J. P. Bonardi and W. L. Barrett. 1920. 35 pp.

TECHNICAL PAPER 270. The detection and estimation of platinum in ores, by C. W. Davis. 1921. 28 pp.

PUBLICATIONS THAT MAY BE OBTAINED ONLY THROUGH THE SUPERINTENDENT OF DOCUMENTS.

BULLETIN 70. A preliminary report on uranium, radium, and vanadium, by R. B. Moore and K. L. Kithil. 1913. 101 pp., 4 pls., 2 figs. 15 cents.

BULLETIN 103. Mining and concentration of carnotite ores, by K. L. Kithil and J. A. Davis. 1917. 124 pp., 14 pls., 6 figs. 25 cents.

BULLETIN 108. Melting aluminum chips, by H. W. Gillett and G. M. James. 1916. 88 pp. 10 cents.

BULLETIN 150. Electrodeposition of gold and silver from cyanide solution, by S. B. Christy. 1919. 171 pp., 8 pls., 41 figs. 25 cents.

BULLETIN 171. Melting brass in a rocking electric furnace, by H. W. Gillett and A. E. Rhoads. 1918. 131 pp., 4 pls., 1 fig. 25 cents.

BULLETIN 173. Manganese; uses, preparation, mining costs, manufacture of ferro-alloys, by C. M. Weld and others. 1920. 209 pp., 13 figs. 30 cents.

BULLETIN 186. Investigations of zirconium, by J. W. Marden and M. N. Rich. 1921. 152 pp., 2 pls., 3 figs. 25 cents.

TECHNICAL PAPER 177. Preparation of ferro-uranium, by H. W. Gillett and E. L. Mack. 1917. 46 pp., 2 figs. 5 cents.

○